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Sorption Studies of a Modified Locust Bean Gum on a Bleached Sulfite Pulp

Vincent A. Russo

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SORPTION STUDIES OF A MODIFIED LOCUST BEAN GUM ON A BLEACHED SULFITE PULP

A thesis submitted by

Vincent A. Russo

B.Ch.E. 1952, Rensselaer Polytechnic Institute
M.S. 1954, Lawrence College

in partial fulfillment of the requirements
of The Institute of Paper Chemistry
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INTRODUCTION AND PRESENTATION OF PROBLEM

Beater adhesives are often employed to produce certain desirable characteristics in the manufacture of various grades of paper and paperboard. Many of these materials enhance fiber-to-fiber bonding, and notable strength improvements may be obtained without the great expenditure of power in refining. Where these materials are used, excessive mechanical damage to the fibers is thus obviated, and, in addition to improvements in strength, papers can be made which have higher porosity, higher opacity, better formation, and better compressibility for printing. Furthermore, with such strength improvements, higher percentages of poorer quality pulps may be used.

While certain beater adhesives work well in the laboratory, mill trials on these same materials often produce erratic results. A number of factors may be responsible for this behavior. Among these, Swanson (1) has mentioned the recirculation of white water for extended periods of time, and the accumulation of fines and fillers. In such mixed systems, a sorption competition may exist among the various components for the added beater adhesive. Where the major portion of the adhesive is sorbed on the fillers and fines present, the effectiveness of the adhesive may be reduced because of poor location in the sheet, satisfaction of the sorption forces of the adhesive, or poor residual adhesion. Knowledge of the basic phenomena involved in the sorption of beater adhesives is needed to better realize their capabilities.

This study was undertaken as a contribution to our understanding of the sorption behavior of polysaccharide beater adhesives. Particular emphasis was placed on the rate aspects of the problem in an effort to characterize the mechanism of the sorption process. As a representative system for this study, a partially methylated derivative of the well-known mannogalactan, locust bean gum, and a commercial bleached sulfite pulp were selected. The effect of the variables time, gum concentration, temperature, degree of agitation, and pulp specific surface area on the rate of gum sorption was investigated.

HISTORICAL REVIEW

The literature on the use of beater and headbox additives has been reviewed up to 1949 by Jayne, Tongren, and Jackson (2), and from 1949 through 1955 by Swanson (1). Specific studies pertinent to this thesis are briefly surveyed in the following paragraphs.

THE RETENTION OF POLYSACCHARIDE BEATER ADHESIVES

Fundamental studies of the sorption behavior of polysaccharide beater adhesives have been limited, primarily because of the difficulty in accurately measuring the retention of these materials.

Two methods for measuring the retention of locust bean gum and methylcellulose were suggested by Shriver, Webb, and Swanson (3). One of these methods, based on the anthrone test for carbohydrates, was colorimetric. This method involved an analysis of the carbohydrate content of the filtered white water before and after sorption of the adhesive. The other technique was viscometric, and involved measurement of the viscosity of the white water before and after sorption. These methods of analysis were indirect, relying on small concentration differences, and therefore subject possibly to relatively large errors. The results of these investigators showed that the sorption values computed by the viscometric method were 50 to 100% greater than those obtained by the anthrone method.

More recently, Keen and Opie (4) described another colorimetric technique for carbohydrate analysis in white water. Their method is

based on the formation of a permanent amber color when a solution of a carbohydrate is treated with color-free phenol and concentrated sulfuric acid. Best results were reported at carbohydrate concentrations in the range of 0 to 25 p.p.m. Here again adhesive retention was determined indirectly, and soluble carbohydrate fractions in the pulp may be a source of error. For example, Most (5) has shown that soluble carbohydrate fractions present in the supernatant solutions of a series of pulp-hemicellulose slurries may vary from 28 to 102 p.p.m.

Leech (6) developed a new analytical method for the determination of locust bean gum in paper. This direct technique was based on an analysis of the galactose content of the paper after gum addition. Gum-treated sheets were hydrolyzed with dilute sulfurous acid, the sugars recovered, separated by paper partition chromatography, and finally determined by oxidation with sodium periodate. This method has proven to be accurate; its disadvantages are its complexity, and the fact that the method is not rapid.

In recent years, the application of radiochemical tagging methods has provided a valuable analytical technique to the study of polysaccharide retention by papermaking fibers. Swanson, Becher, and Dickey (7) tagged locust bean gum with carbon^{14}, and determined the sorption of the labeled gum on papermaking fibers and pulp fines. Tagged locust bean gum was prepared by reacting the sodium derivative of the gum, prepared according to Gaver (8), with carbon^{14} methyl iodide. A thin-window Geiger-Mueller counter was used for the radiochemical measurements. In an

experiment designed to study the distribution of the slightly methylated gum between paper fibers, fines, and white water, only 75 to 85% of the added gum was recovered. Subsequently, with a Bernstein-Ballentine (9) proportional counter technique, Most (10) showed that the Geiger-Mueller thin window method gave results which were about 15% too low. The proportional counting technique obviates the difficulties of low efficiency counting in the solid state by employing radioactive analysis in the gaseous phase.

A modified Kiliani cyanohydrin synthesis has been described by Isbell (11) as a means of tagging polysaccharide molecules. Most (5) utilized this method to label certain slash pine hemicelluloses with carbon^{14}, and investigated the sorption of these fractions on cellulose fibers. The amount of sorbed hemicellulose on the fibers was determined directly by completely oxidizing the pulp-sorbed hemicellulose samples to gaseous products, and then measuring the carbon^{14} radioactivity by proportional counting. The samples were oxidized by the wet combustion technique of Van Slyke and Folch (12). This radiochemical approach to the measurement of polysaccharide retention possesses a number of advantages; the method is direct, analyses are rapid, and a high degree of precision is possible.

SORPTION STUDIES OF POLYSACCHARIDES BY CELLULOSE FIBERS

The sorption of water-soluble cellulose ethers by cotton linters, bleached and unbleached sulfite, and bleached and unbleached kraft pulps has been studied by Shriver (13). Sorption was found to increase three to

four times from unbeaten to well-beaten pulps, and required 100 to 180 hours for completion. The sorption rate was also found to be a function of the initial adhesive concentration. The sorption was irreversible with respect to isothermal concentration changes, but exhibited a temperature hysteresis. Some desorption occurred when the temperature at equilibrium was decreased from 38 to 3.3°C. With increasing temperature, sorption was found to increase, and Shriver postulated the retention mechanism involved a combination of gelation and true adsorption.

Pearl (14) has studied the sorption and rate of sorption of the amylose fraction of starch by papermaking fibers. This system was characterized by an initially high rate of sorption, which gradually decreased with time. Sorption continued until all the amylose in solution had been sorbed. Complete exhaustion of the amylose in solution required times up to 600 hours at 25°C. When the amylose concentration was maintained, the rate of sorption decreased rapidly at first, and then appeared to approach a constant value. The rate of sorption increased with a decrease in temperature. Sorption was irreversible with respect to concentration, and the amylose only partially removed by an increase in temperature. The sorption rate at pH 10.4 was much lower than that at pH 4. With higher amylose concentrations, and with increased beating of the pulp, the rate of sorption was found to increase. The mechanism of sorption was explained as a dual process, in which the amylose was sorbed by the cellulose surface, and this amylose sorbed additional amylose. Pearl termed this process "retrogradation sorption", and suggested that hydrogen bonding was the force holding the sorbed amylose molecules to the fiber and to each other.

The sorption of four slash pine hemicellulose fractions by a bleached sulfite pulp was studied by Most (5). For each of the four fractions, the initial rate of sorption was relatively high. Higher sorption rates were noted for the hemicelluloses having the higher mannan contents. The sorption rates decreased markedly after about 10 hours, with the sorption continuing slowly at an almost constant rate, without reaching equilibrium in 10 days. Sorption was found to be irreversible with respect to concentration over a wide range of sorption levels. Among the hemicelluloses differences in the direction of response to a temperature increase of 15°C. were found. The sorption of two fractions was unaffected by the temperature change; for one it increased, and for another it decreased. The sorption rate at pH 10 was 25 to 40% greater than that at pH 4.5. —? should be reversed Lowering the consistency of the pulp slurry increased the specific sorption. This increase at low pulp consistencies was attributed to a combination of higher sorbate concentration and an increased fiber surface availability. As in the work of Pearl (14) with amylose, Most postulated a multilayer retention mechanism involving the deposition of hemicellulose on the fiber, followed by hemicellulose on hemicellulose sorption.

Further evidence of irreversibility in the sorption of polysaccharides by cellulose fibers was reported by Yllner and Enström (15). These investigators studied the sorption of pentosans removed from birch and spruce wood during the early stages of a kraft cook. The pentosans were sorbed from the cooking liquor on cotton, cotton linters, and bleached sulfite fibers. The sorption was irreversible with respect to concentration and some 20% of the sorbed pentosans were not removed by a one-hour

extraction with 10-20% caustic solutions at 20°C. The amount sorbed increased with time, parallel to the increase in pentosan concentration in the liquor. Sorption stopped only when the pentosan content of the liquor dropped to "negligible levels".

Very little of a fundamental nature has been done in the study of the sorption mechanism of the natural mannogalactans, guar and locust bean gum. Some preliminary work has been done by Webb, Morse, and Swanson (16), but these studies can only be considered qualitative because of the limitations of the anthrone colorimetric technique employed. The initial sorption of locust bean gum was found to be rapid, reaching an apparent equilibrium in about 30 minutes. At concentrations of 0.5 to 2.0% locust bean gum based on the fibers, retentions of about 96% of the added gum were found at the end of one hour. However, due to a filtration error caused by soluble carbohydrate fractions in the pulp, these values are probably not absolute. Temperature did not seem to affect the sorption. Handsheets made at 4 and at 70°C., with the same amounts of locust bean gum added, had the same burst strength. No detectable gum desorption was found from a sorbed pulp subjected to Soxhlet extraction with distilled water for 48 hours.

Further indication of the irreversibility of locust bean gum sorption is noted from the work of Leech (6). Washing handsheets made from pulp to which 5% gum had been added did not alter their strength properties relative to comparable unwashed sheets.

Gruenhut (17) studied the retention of mannogalactan gums by means of the differential viscosity method suggested by Shriver, et al. (3). She reported that the rate of sorption of locust bean gum is dependent on solution concentration, and therefore concluded that the sorption takes place on the surface of the fiber. In contrast to the work of Webb, Morse, and Swanson (16), the sorption of locust bean gum was reported as affected by temperature. The strength of handsheets made at 4.2°C. was greater than the strength of those made at usual temperatures. Gruenhut therefore concluded that gum sorption increased as temperature decreased. She also noted that sorption decreased significantly with dilution of the gum-pulp slurry, but increased as pH was lowered. The sorption of locust bean gum was reported as more rapid than that of guar because of its less highly branched structure.

The sorption of guar gum on boxboard and bleached kraft pulp has been studied by Keen and Opie (4). Sorption appeared to take place quickly with minor or no changes observed in the guar sorbed after 5 minutes regardless of guar concentration. Gum sorption was only slightly dependent on gum concentration, with a definite limit to the quantity of guar which could be sorbed. The authors suggest that a level of saturation exists which is perhaps dependent upon pulp specific surface area. As the degree of beating was increased, the amount of guar sorbed by both the boxboard and kraft pulps increased. Guar sorption decreased with a decrease in pulp consistency, although the difference was not great over the range of solids from 1.0 to 0.32%. Maximum sorption occurred at approximately neutral pH; it was at its lowest under alkaline conditions.

An accurate determination of the effect of temperature on sorption was not made. Preliminary data at 20 and 50°C. indicated that only minor changes in sorption occurred with changes in temperature.

In summary, a review of the literature reveals gaps in our understanding of the sorption behavior of polysaccharide beater adhesives. Irreversibility of sorption has been noted, and a multilayer sorption process is indicated, at least in the case of starch and the hemicelluloses. The role of temperature is not clear, and without proper analytical techniques, hypotheses and conclusions have been made on very limited, and often questionable data. Fundamental rate and equilibrium studies have been limited, and no consideration has been given to the transport phenomena involved. Basic studies of the locust bean gum-pulp system are especially lacking; this present research was undertaken to elucidate the nature of the phenomena involved, and thus contribute to our understanding of the over-all sorption process.

APPROACH TO THE PROBLEM

Analysis of sorption studies in the past has been complicated by the fact that the concentration of sorbate varied markedly during the course of the sorption experiment. In these present studies, it was believed that the sorption mechanism could be better evaluated by eliminating this concentration effect by use of a so-called "infinite bath technique". This approach necessitates a direct means of retention analysis.

Direct determination of the sorbed gum was achieved by means of a radiochemical tagging technique. Purified locust bean gum was labeled by partial methylation with carbon^{14} methyl iodide. It is the sorption of this partially methylated gum (PMG) which is the subject of these investigations.

The over-all PMG sorption phenomenon may be considered as a complex heterogeneous process. As such, the removal of PMG from solution might be thought of as taking place in a series of steps. One or more of these may be involved as rate determining in an analysis of the over-all process. Knowledge of the factor or factors involved should do much to elucidate the basic nature of the sorption phenomenon. In the PMG-pulp system, the following steps might be considered:

1. Diffusion or transport of PMG from the bulk of the solution to the surface of the fiber
2. PMG adsorption at the fiber surface
3. PMG diffusion into the fiber
4. The reverse of Steps 1 through 3

In this research, the complexities of Step 4 were obviated. In the first place, for all practical purposes, the sorption of PMG is essentially irreversible; and secondly, this complication was avoided by approaching the problem with studies of initial rate. Similarly, diffusion into the fiber (Step 3), while possible, is not believed to occur to any appreciable degree because of the relative size of the gum polymer and that of the pores and interstices present in the pulp fibers (18-21). Significant migration of the PMG molecules into the fiber would have to be endwise, and it is difficult to conceive that this can occur to any appreciable extent. As Shriver (13) pointed out for the sorption of methylcellulose:

> "It seems relatively unlikely, that...[the polymer]... could penetrate such a structure more than superficially since, even if chain ends were to penetrate the cellulose (like threading a needle), the ends would soon meet cellulose spaces of the same magnitude as the molecular diameter."

Similar conclusions were reached by Pearl (14) in studies of amylose sorption, and Most (5) with the hemicelluloses of slash pine.

This research, therefore, reduced itself to a consideration of a diffusional transport process (Step 1) and adsorption proper on the fiber surface (Step 2). Either or both of these processes might have been involved as rate determining in the over-all sorption phenomenon. It was believed that an understanding of this system could best be approached by consideration of a number of experimental observations. The effect of the variables time, PMG concentration, temperature, degree of agitation, and pulp specific surface area on the rate of PMG sorption was investigated.

NOMENCLATURE

SORPTION TERMS

Sorption -- the process by which material is removed from solution or dispersion by a solid or liquid surface. Use of this term suggested by McBain (22) to avoid precommitment to either adsorption or absorption.

Sorbate -- the substance which is taken up by a surface.

Sorbent -- the material upon which sorption takes place.

RADIOACTIVITY TERMS

d/m -- disintegrations per minute

mc. -- millicurie, 2.22×10^9 disintegrations per minute

μc. -- microcurie, 2.22×10^6 disintegrations per minute

mμc. -- millimicrocurie, 2.22×10^3 disintegrations per minute

c.p.m. -- counts per minute; in this study taken as disintegrations per minute because 98-99% counting efficiency is obtained with the technique employed.

Specific activity -- the radioactivity per unit weight or volume of material, expressed in any radioactivity units, e.g., c.p.m./mg., mμc./mg.

PULP FRACTIONS

C-I -- pulp beaten 20 minutes in Valley beater, fines removed, hydrodynamic specific surface area, 9260 sq. cm./g.

C-II -- pulp beaten 35 minutes in Valley beater, fines removed, hydrodynamic specific surface area, 11,780 sq. cm./g.

C-III -- pulp beaten 50 minutes in Valley beater, fines removed, hydrodynamic specific surface area, 15,610 sq. cm./g.

C-IV -- pulp beaten 75 minutes in Valley beater, fines removed, hydrodynamic specific surface area, 29,900 sq. cm./g.

PREPARATION OF MATERIALS

The two primary materials for this study were purified locust bean gum (LBG) and a Weyerhaeuser standard bleached sulfite pulp.

PURIFICATION OF LOCUST BEAN GUM (LBG)

The LBG for this investigation was purified from a commercial crude product according to a procedure described by Leech (6). In essence, this method involved the solution of the impure gum in hot water, centrifugation to remove undissolved constituents, precipitation of the gum into alcohol, and drying by solvent exchange. The resulting product was thoroughly mixed and sampled for characterization by the method of quartering. The writer is indebted to the Analytical Department of The Institute of Paper Chemistry for performing these analyses. The results are summarised in Table I.

TABLE I

CHARACTERIZATION OF CRUDE AND PURIFIED LBG

	Ash,[a] %	Nitrogen,[a] %	Carbon,[a] %
Crude LBG	0.85	0.85	---
Purified LBG	0.27	0.29	41.97

[a] Based on oven-dry samples

PREPARATION AND ANALYSIS OF PULP

A Weyerhaeuser standard bleached sulfite pulp was used in all the studies reported in this research. This pulp was obtained directly after the last press of the pulp machine, and was received in sheet form in an undried condition. Prior to storing, the pulp was broken up from its sheet form by passing it through a laboratory pulp breaker. It was then thoroughly mixed, placed in double polyethylene bags and stored at 5°C., with 1% formaldehyde as a preservative.

For the sorption studies a series of beaten pulps were prepared. The bleached pulp was beaten in a laboratory Valley beater for intervals of 20, 35, 50, and 75 minutes, and then classified to remove fines and fiber debris. A Bauer-McNett classifier with 8, 16, 65, and 150-mesh screens was used for the removal of fines. The classified pulp yields are presented in Table II.

A portion of the original unclassified pulp at each beating interval was retained for analysis. The pulps were dewatered, placed in double polyethylene bags and stored at 5°C., with 1% formaldehyde as a preservative.

For both the classified and unclassified pulps, the fiber properties of hydrodynamic specific surface area, and swollen specific volume were determined by the constant rate filtration technique of Ingmanson (23). These analyses were performed by the Pulping Group of The Institute of Paper Chemistry. The results are given in Table II.

Details of the pulp preparation and analysis are presented in Appendix I.

TABLE II

SUMMARIZED PULP PROPERTIES

	Refining Time, min.			
	20	35	50	75
Classified yield, after removal of fines, %	86.8	81.1	79.5	71.0
Schopper-Riegler freeness, cc.				
Unclassified	810	700	525	350
Hydrodynamic specific surface, sq. cm./g.				
Classified	9260	11,780	15,610	29,900
Unclassified	15,300	24,000	46,000	73,900
Wet fiber specific volume, cu. cm./g.				
Classified	2.39	2.45	2.57	2.80
Unclassified	2.58	2.78	2.60	2.77

PRELIMINARY EXPERIMENTAL STUDIES

PMG SORPTION MEASUREMENTS

PRINCIPLE OF METHOD

In the past, studies of the sorptive behavior of polysaccharide beater adhesives have been difficult because of the lack of a reliable and rapid method for determining the extent of sorption. With the exception of Leech's chromatographic technique (6), the analytical methods employed have been indirect and subject to considerable criticism. More recently, the use of radiochemical tagging techniques has provided a convenient direct means for analyzing polysaccharide retention by papermaking fibers.

By introducing radioactive carbon-14 into the LBG molecule, as accomplished by Swanson, Becher, and Dickey (7), the sorption of gum on pulp samples may be determined directly by an analysis of the radioactivity present. In using this technique the radioactive or labeled gum is not used singly, but is diluted with unlabeled gum to a known level of specific activity. This conserves the quantity of radioactive material and facilitates handling, but may introduce a complicating factor. If there is any selective sorption between the labeled and unlabeled components, sorption determinations by radioactive counting would apply only to the labeled material. Therefore, prior to applying this technique for sorption measurements, it is essential that no sorptive difference exist between the labeled and unlabeled material, or that the extent of any such difference be known quantitatively.

In this research, successful tagging of the LBG molecule was accomplished by partial methylation with carbon^{14} methyl iodide. The details of this procedure will be discussed later, in Appendix IV, and it will be shown that the labeling reaction affected the sorptive behavior of the LBG. In mixtures with the original unmethylated gum as a diluent, a preferential sorption effect was noted. For the purposes of this study, this problem was resolved by a partial methylation of the diluent LBG as well as the tagged material. Nonradioactive methyl iodide was used for the diluent gum, and this methylation was carried out to the same degree as in the labeling reaction. In essence, therefore, the sorbate in this investigation is a partially methylated locust bean gum, PMG.

THE MANOMETRIC DETERMINATION OF CARBON AND ITS RADIOACTIVITY

To obviate the difficulties of low efficiency counting in the solid state, it is convenient to determine the radioactivity of the sorbed PMG in the gaseous phase using the Bernstein-Ballentine (9) proportional counting system. The solid pulp samples were converted to gaseous products by the wet combustion technique of Van Slyke and Folch (12) as modified for use with radioactive carbon samples by Van Slyke, Steele, and Plazin (24). Essentially, the method involves the oxidation of the pulp sample completely to carbon dioxide, absorbing the gases in alkaline hydrazine solution, separating the carbon dioxide from the other liberated gases, collecting it in a proportional counting tube, diluting with methane, and counting the radioactivity present. The use of the Van Slyke combustion is especially convenient in that it permits one to determine the sorption per unit

weight of pulp without the need for a separate measurement of sample size. The sample size used in the analysis is calculated from a manometric determination of the total evolved carbon dioxide prior to transferring the gas to the proportional counting tube. Details of this calculation are given in Appendix V.

CALIBRATION OF THE PROPORTIONAL COUNTING TUBES

In using a proportional counting tube for the measurement of radioactivity by the Van Slyke technique, two characteristics of the tube must be known. These are the nature of its counting plateau, and the effect of the partial pressure of the total carbon dioxide present on the counting efficiency.

The counting plateau of a proportional counting tube is that portion of the curve of counting rate versus applied voltage which shows a minimum slope over a range of voltages. In this region, small changes in applied voltage will have little effect on the counting rate.

In proportional counting tubes, with mixtures of radioactive and non-radioactive carbon dioxide in methane, it has been demonstrated that the counting rate depends to a certain extent on the partial pressure of the total carbon dioxide present. For proportional counting tubes of 100-ml. volume, Van Slyke, Steele, and Plazin (13) noted that the efficiency of counting was constant up to a partial pressure of about 120 mm. Hg. for the carbon dioxide, or approximately 7 mg. of total carbon. At greater levels of carbon dioxide the efficiency factor dropped off; for example, at 15 mg.

of total carbon, the counting rate for a constant level of radioactivity had decreased about 5%.

Both of the above characteristics were obtained for three proportional counting tubes purchased from Nuclear Instrument and Chemical Corporation of Chicago, Illinois. Details of the calibration experiments are given in Appendix II.

LABELING LBG WITH CARBON^{14}

At the outset of this study, two approaches to the radiochemical labeling of LBG appeared promising. These were the modified Kiliani synthesis employed by Isbell (11), and the partial methylation technique suggested by Swanson, Becher, and Dickey (7).

LABELING TRIALS WITH CARBON^{14} SODIUM CYANIDE

The initial approach taken here was that of Isbell (11). It had been successfully applied by Most (5) in the labeling of four fractions of slash pine hemicellulose, and was not expected to affect the sorptive characteristics of the labeled LBG.

These initial trials to label LBG with carbon^{14} sodium cyanide were not satisfactory. The extent of labeling was much lower than was anticipated, and the radiochemical yield was a prohibitively low 1%. Contrary to the published data of Isbell (11), who reported a D.P. of about 200 for locust bean meal, these results indicate that this LBG product is a very high polymer, with a D.P. of about 3000 to 4000, containing few reducing

end groups. Without a greater number of these groups, effective labeling by a cyanohydrin synthesis is impractical.

In an effort to increase the combining power of the LBG, without major alterations in the molecule, the effect of a mild hydrolysis on the gum prior to the labeling was investigated. Treatment with 2% sulfuric acid at 25°C. for 72 hours produced no detectable increase in combining power. Further hydrolysis experiments were originally planned; however, because of time limitations, it was considered more expedient to abandon this approach, and to label LBG with carbon^{14} by employing the alternate methylation technique of Swanson, Becher, and Dickey (7).

Details of these initial labeling trials are presented in Appendix III.

LABELING BY METHYLATION WITH CARBON^{14} METHYL IODIDE

Successful labeling of LBG with carbon^{14} was accomplished by partial methylation with radioactive methyl iodide. The sodium alcoholate of LBG was first formed, and then refluxed for 8 hours with carbon^{14} methyl iodide. Four labeled LBG products were prepared containing various levels of radioactivity. These were purified by dissolving in distilled water, and then recovered by precipitating into absolute alcohol. Details of the methylation experiments are given in Appendix III. The results of the labeling reactions are summarized in Table III.

The methylation labeling procedure for LBG was originally relegated to the position of a secondary approach because it introduces methoxyl

groups into the polymer at the expense of a portion of the original hydroxyl groups present. It was believed that this modification might produce a labeled LBG product with different sorptive characteristics than those of the original LBG. This proved to be the case. The sorption characteristics of mixtures of methylated labeled LBG and unmethylated LBG were studied, and a preferential sorption effect was noted. The unmethylated nonradioactive LBG was sorbed to a greater extent than the methylated radioactive product. Details of this investigation are given in Appendix IV.

The preferential sorption effect noted above was obviated by methylating the diluent LBG with nonradioactive methyl iodide to essentially the same methoxyl content as the labeled gum. In all, 71 grams of diluent gum were prepared with a methoxyl content of 6.25%.

DEVELOPMENT OF INFINITE BATH CONDITIONS

From calculations based on the LBG sorption data of Leech (6), it was believed that infinite bath conditions could be approached by working at a very low pulp consistency, 0.01%, and high gum concentration, 0.10 g./l. The effect of time on the initial bath conditions with the sorption of PMG was studied by preparing a series of individual PMG-pulp systems in 500-ml. wide-mouthed screw-capped bottles. Pulp C-IV, the most highly beaten pulp planned for use in this study, was the sorbent in this experiment. This pulp had a hydrodynamic specific surface area of 29,900 sq. cm./g., and thus provided the most extreme conditions of test.

TABLE III

RADIOACTIVE LBG PRODUCTS

	Run I		Run II		
	LBG-Ia	LBG-Ib	LBG-IIa	LBG-IIbc[a]	Blend of LBG-Ib & LBG-IIbc
Yield, g.	1.5	1.3	2.8	3.0	4.3
Yield, radiochemical,[b] %	23.9	7.6	28.9	5.1	----
Specific activity, mμc/mg.	159	58	103	17	29
Methoxyl, calculated,[c] %	5.88	---	5.94	---	-----
Methoxyl,[d] %	----	---	6.15	---	5.75

[a] Composite blend of products LBG-IIb and LBG-IIc.
[b] Yield based on original radioactivity added in form of $C^{14}H_3I$.
[c] Calculation based on the radioactivity of product and initial reactants.
[d] Microanalysis performed by Huffman Microanalytical Laboratories, Wheatridge, Colorado.

Briefly, the experimental procedure consisted of adding aliquots of PMG solution to 50-mg. samples of the pulp in screw-capped bottles, agitating gently in a thermostated bath at 25°C., recovering the sorbed pulp at selected time intervals by filtration, washing, and then analyzing for PMG retention by the wet combustion technique previously described. Details of the sorption-time experiment will be discussed under EXPERIMENTAL PROCEDURES in a following section of this thesis. The results of this experiment are presented in Table IV and Figures 1a and 1b.

From Figure 1a and especially in Figure 1b, it will be noted that the sorption of PMG increased continually throughout the course of the sorption experiment. Although the rate of sorption decreased with increasing time, the sorption of gum showed no indication of leveling off.

TABLE IV

EFFECT OF TIME ON SORPTION

Beaten Pulp C-IV, 29,900 sq.cm./g.
Pulp Consistency, 0.0167%
Initial PMG Concn., 0.100 g./l.
pH, 6.5

Time, min.	PMG Specific Sorption x 10^2,[a] g./g. pulp	Calculated Residual PMG Concn., g./l.	Decrease In PMG Concn., %
1	0.678	0.0989	1.1
2	0.921	0.0985	1.5
4	1.18	0.0980	2.0
8	1.38	0.0977	2.3
15	1.72	0.0970	3.0
45	2.68	0.0955	4.5
135	3.67	0.0938	6.2
405	5.17	0.0914	8.6
840	6.13	0.0898	10.2
1680	7.13	0.0881	11.9
3360	8.12	0.0865	13.4
6720	9.05	0.0849	15.1

[a] Average of duplicate analyses

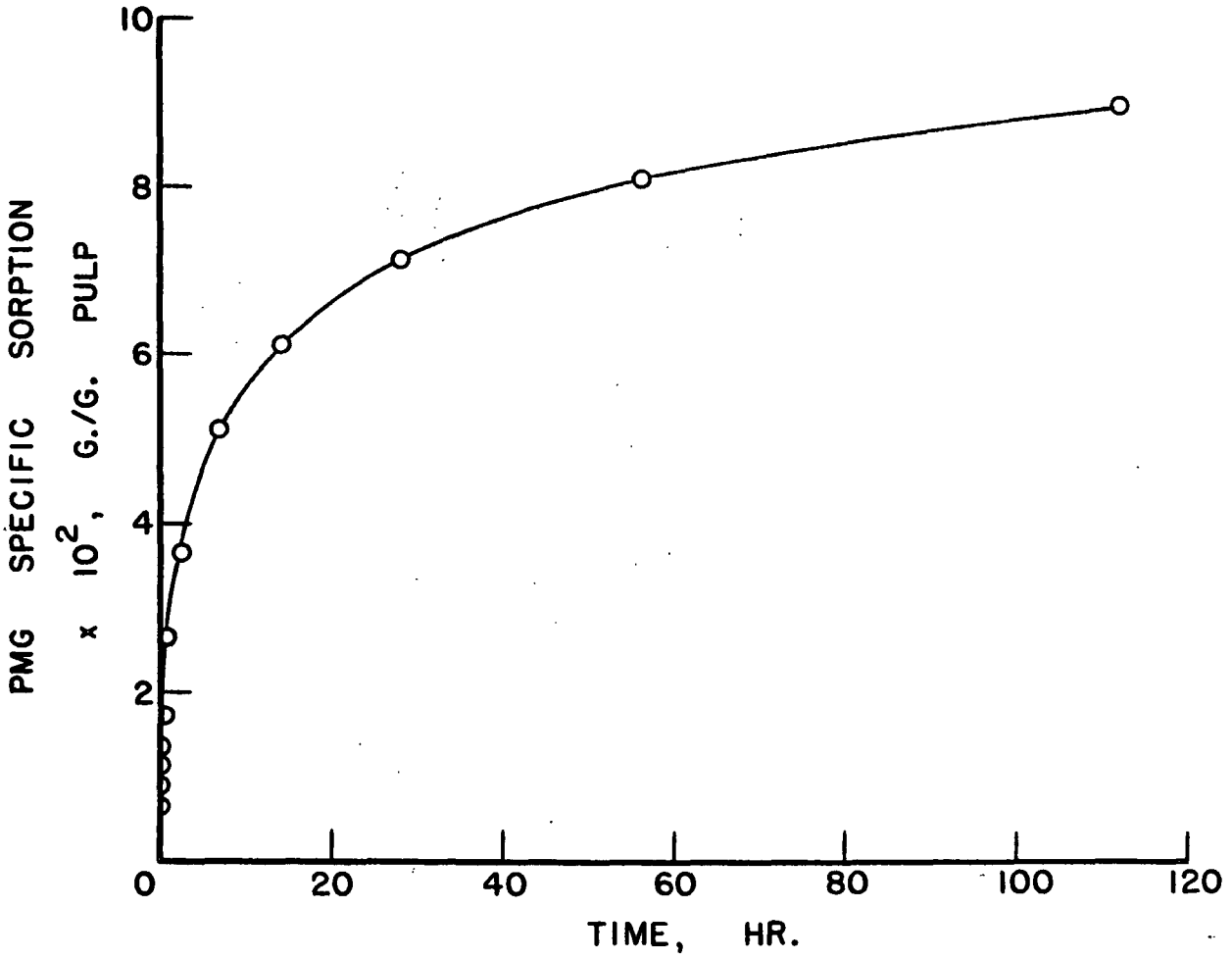

Figure 1a. PMG Sorption as a Function of Time

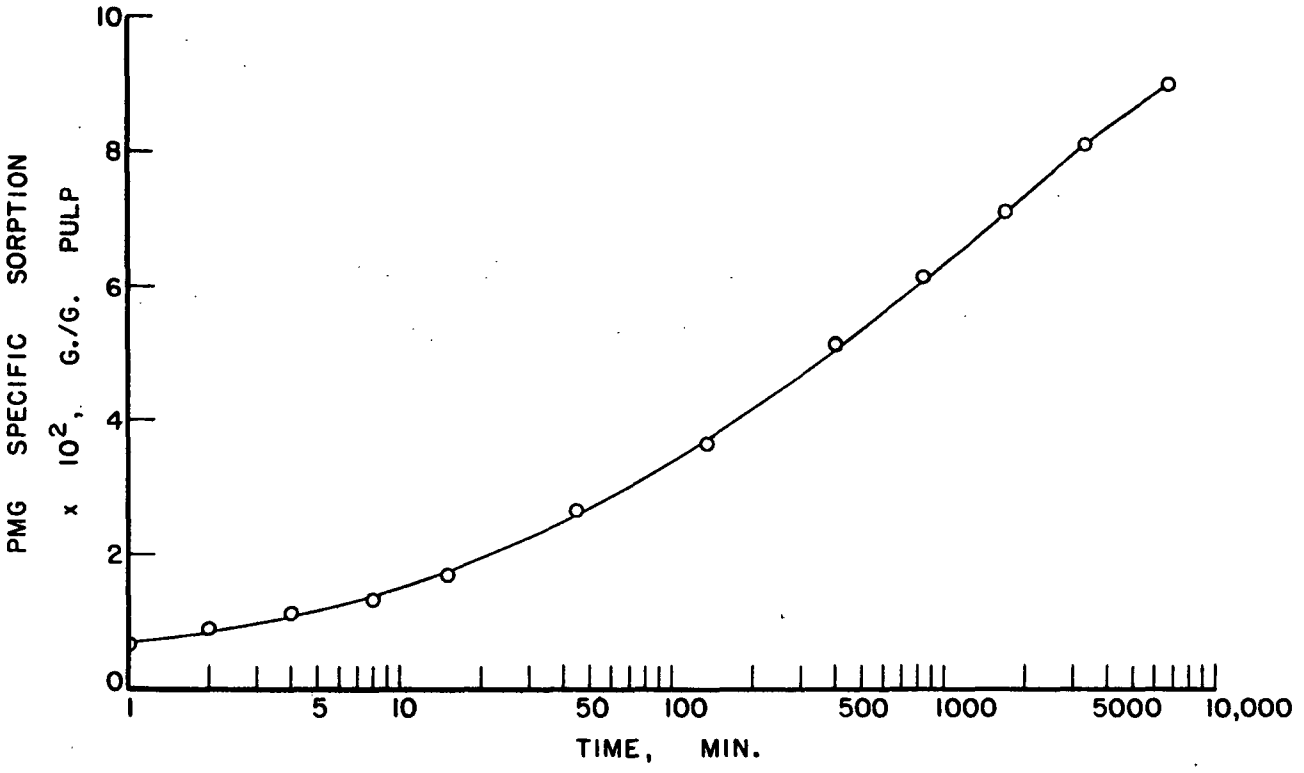

Figure 1b. PMG Sorption as a Function of Time

A condition of sorption equilibrium was not achieved in 112 hours. It is probable that at least a part of the decrease in sorption rate is due to the fairly rapid breakdown of infinite bath conditions. In 45 minutes, a 5% decrease in initial PMG concentration was noted, and over the course of the sorption experiment the total decrease amounted to 15%. If the sorption experiment had been extended beyond 112 hours, it is believed that the breakdown in initial bath conditions may have been even greater. PMG sorption may have continued until the supply of gum was exhausted without reaching a condition of sorption equilibrium. Such behavior was observed by Pearl (14) for the sorption of amylose on pulp fibers.

In view of these findings, rather than pursuing the question of equilibrium further, it appeared more fruitful to consider the sorption phenomena solely from an initial rate standpoint. Over the first 15 minutes of sorption the change in initial sorption conditions amounted to only 3%, and therefore an infinite bath condition was approached. With a pulp of lower specific surface, it was believed that the change in PMG bath concentration expected would be less and therefore even more suitable for subsequent rate studies. This proved to be the case. In Table V are presented the results of PMG sorption on pulp C-II using the same conditions for the sorption experiment as those previously used for Pulp C-IV. The hydrodynamic specific surface area of Pulp C-II was 11,780 sq.cm./g.

TABLE V

EFFECT OF TIME ON SORPTION

Beaten Pulp C-II, 11,780 sq.cm./g.
Pulp Consistency, 0.0167%
Initial PMG Concn., 0.0100 g./l.
Temperature, 25°C.
pH, 6.5

Time, sec.	PMG Specific Sorption x 10^2, g./g. pulp	Calculated Residual PMG Concn., g./l.	Decrease In PMG Concn., %
60	0.438	0.0993	0.7
120	0.583	0.0990	1.0
200	0.722	0.0988	1.2
300	0.838	0.0986	1.4
900	1.234	0.0979	2.0

Over a 15-minute interval, the decrease in PMG concentration was limited to only 2%. It will be shown later from studies of the effect of concentration on rate, that changes of this magnitude are not significant.

THE DESORPTION OF PMG FROM SULFITE PULP FIBERS

As was mentioned above, upon completion of a sorption experiment the pulp fibers are recovered by filtration for analysis. In order to eliminate the necessity of correcting for unsorbed PMG solution in the fibers so recovered, it is desirable to wash them free of this residual solution by successive dilutions with water. Obviously, this technique could not be employed if desorption were to occur during washing. The following

experiment was performed to determine the effect of isothermal dilution on LBG retention.

The 112-hour sorption sample from the orienting sorption experiment on Pulp C-IV was divided approximately in half. One portion was dried and analyzed for PMG retention. The other portion was resuspended in 300 ml. of distilled water, and returned to the thermostated water bath where it was agitated. From the sample bottle, 2-ml. aliquots of the distilled water were withdrawn at 1-hour, 24-hour, and 96-hour intervals, and the pulp itself was recovered after 96 hours of desorption. The aliquots were evaporated to dryness, and analyzed for PMG by wet combustion and radioactive counting. These results are presented in Table VI.

TABLE VI

DESORPTION EXPERIMENT
ANALYSES OF ALIQUOTS OF DISTILLED WATER

Desorption Time, hours	Aliquot Radioactivity, c.p.m./2 ml.	Calculated Total PMG Desorption, %
1	0	0
24	0	0
96	7-9	4.1

In the aliquots of distilled water, no detectable radioactivity was noted for the 1 and 24-hour samples, and only 7-9 c.p.m. above background for the sample at 96 hours. At this low level of radioactive counting, the precision of measurement suffers; however, based on this figure an

estimate can be made of the total desorption after 96 hours in distilled water. This amounts to a 4.1% decrease in the retention of PMG based on the fiber.

A comparable figure for desorption was determined by direct analysis of the pulp fibers before and after 96 hours of desorption. The results of these analyses are presented in Table VII.

TABLE VII

DESORPTION EXPERIMENT
ANALYSES OF PULP FIBERS

PMG Specific Sorption x 10^2, g./g. pulp

	Before Desorption	After 96-Hr. Desorption	Calculated Total PMG Desorption, %
	8.98	8.76	2.5
	9.11	8.68	4.7
Av.	9.05	8.72	3.6

Considering the extreme condition of this experiment, these results indicate that no significant desorption of PMG occurs during the washing procedure. Only after protracted contact with distilled water was a detectable PMG desorption noted, and it must be remembered that this was for pulp fibers containing a very high level of sorbed gum. These conclusions are supported by unpublished data of Webb, Morse, and Swanson (16). These investigators found no detectable LBG desorption from an LBG-sorbed pulp sample subjected to Soxhlet extraction with distilled water for 48 hours.

SORPTION-TIME EXPERIMENTS

EXPERIMENTAL PROCEDURES

PREPARATION AND ANALYSIS OF PMG STOCK SOLUTIONS

For the sorption experiments, stock solutions of PMG were prepared containing blends of radioactive material. The amount of radioactive gum present represented 10-20% of the total. The dry materials were weighed on an analytical balance, mixed together, and then dispersed in distilled water. Dispersion of PMG required great care; the dry materials were slowly sprinkled into vigorously stirred distilled water. The mixture was then heated to 85°C. while the stirring was continued. Five to ten minutes at this temperature was sufficient to disperse the bulk of the gum. Any stray material or undispersed gum particles were removed by filtering through a plug of glass wool. To inhibit microbiological attack the filtered dispersion was stored in the refrigerator and used shortly after preparing.

Two-milliliter aliquots of the stock solution were pipetted into combustion tubes for analysis of the PMG concentration and specific activity. These aliquots were evaporated to dryness overnight in a vacuum desiccator, oxidized by wet combustion, and the radioactivity determined. Duplicate analyses were performed on each stock solution. The results are summarized in Table VIII.

The standard deviation of the PMG concentration analysis, based on the duplicate analyses, was calculated to be $\pm$ 0.005 mg./ml. At the 90% level

TABLE VIII

PMG STOCK SOLUTION ANALYSES

Stock Solution No.	Concn., mg./ml.	Specific Activity, c.p.m./mg.
PMG-1	2.538	19,001
	2.544	19,177
PMG-2	1.436	43,100
	1.440	43,500
PMG-3	2.564	20,054
	2.579	20,339
PMG-4	1.990	47,000
	1.990	47,000
PMG-5	1.470	42,500
	1.455	42,200

of significance, the confidence interval for this analysis would be ± 0.03 mg./ml. On a percentage basis, taking into account the magnitude of the concentration analysis, the confidence interval range would extend ± 1 to 2%.

For the specific activity determination, the calculated standard deviation was ± 134 c.p.m./mg. Again at the 90% level of significance, the confidence interval for the specific activity determination would extend ± 856 c.p.m./mg. This represents a range of confidence limits from ± 1.8 to 4.5%.

DETAILS OF THE SORPTION-TIME EXPERIMENTS

In the sorption experiments, separate samples were prepared for each

time interval. These samples were identical in all respects. Fifty-milligram samples of pulp were prepared volumetrically by taking 100-ml. aliquots for a pulp suspension of 0.05% consistency. A measured volume of PMG was then introduced and the sorption experiment conducted. The detailed procedure was as follows.

Sufficient wet pulp for the sorption experiment was weighed on an analytical balance and then dispersed by gentle shaking in a small volume of distilled water contained in a Mason jar. Additional distilled water was then added to adjust the consistency to 0.05%. After standing overnight to be sure that equilibrium had been achieved, 100-ml. aliquots were taken and placed in 500-ml. wide-mouthed screw-capped bottles. The sample bottles were then closed and placed in a controlled temperature water bath.

After the temperature of the pulp slurry reached that of the controlled water bath, a measured volume of PMG solution, similarly heated (or cooled), was introduced, and the sorption experiment conducted for a predetermined interval of time. Throughout the sorption run, gentle agitation was provided. Samples were placed on a drum rotating at 12 r.p.m. within the controlled temperature water bath. To provide for very rapid mixing of the PMG and the pulp slurry, aliquots of the stock PMG solution were diluted with water to a total volume of 200 ml. before adding to the pulp samples. This technique was investigated by using a copper sulfate solution, and mixing was noted as practically instantaneous.

At the conclusion of a sorption experiment, the pulp fibers were recovered by filtration and the residual PMG solution removed by washing with distilled water. The pulp and residual PMG solution were poured into a coarse-grade fritted-glass funnel, and suction applied to remove the bulk of the residual gum solution. Distilled water at the same temperature as that of the sorption experiment was then added, the pulp pad broken up, and the resulting pulp suspension vigorously stirred as suction was applied. This procedure was repeated with two successive 200-ml. portions of water. The resulting pad of wet pulp was then removed from the funnel, and dried in a vacuum desiccator over magnesium perchlorate prior to analysis for PMG retention.

REPRODUCIBILITY OF SORPTION-TIME EXPERIMENTS

Obviously essential to any research is the ability to reproduce or duplicate experimental results. In the present study two types of reproducibility were considered. The reproducibility of both the individual PMG sorption analyses themselves, and of the over-all sorption-time experiments was studied.

Data illustrating the reproducibility of the PMG sorption analyses are presented in Tables IX and X. Table IX contains the results of two sorption runs on Pulp C-II, while in Table X are presented the results of sorption runs on Pulp C-IV.

The standard deviation for the analyses in Table IX was calculated to be $\pm$ 4 x 10^{-5} g./g. pulp. At the 90% level of significance, the

TABLE IX

REPRODUCIBILITY OF PMG SORPTION ANALYSES

Pulp Fraction C-II, 11,780 sq.cm./g.
Pulp Consistency, 0.0167%
Temperature, 25°C.
pH, 6.5

PMG Concn., g./l.	Time, sec.	PMG Specific Sorption x 10^3, g./g. pulp
0.100	60	4.37
		4.40
	120	5.83
		5.82
	200	7.24
		7.19
	300	8.40
		8.36
	900	12.38
		12.30
0.050	60	3.08
		3.13
	120	4.32
		4.41
	180	4.91
		4.88
	300	5.93
		5.83
	600	7.55
		7.51
	900	9.38
		9.46

TABLE X

REPRODUCIBILITY OF PMG SORPTION ANALYSES

PMG Concn., 0.100 g./l.
Pulp Fraction, C-IV, 29,900 sq.cm./g.
Pulp Consistency, 0.0167%
Temperature, 25°C.
pH, 6.5

Time, min.	PMG Specific Sorption x 10^2, g./g. pulp Run A	Run B
15	1.72	1.84
	1.72	1.82
45	2.67	2.71
	2.68	2.77
135	3.68	3.69
	3.65	3.72
405	5.15	5.23
	5.19	5.30
840	6.13	----
	6.12	----
1680	7.12	----
	7.14	----
3360	8.10	----
	8.15	----
6720	8.98	----
	9.11	----

calculated confidence interval extends $\pm$ 2.4 x 10^{-4} g./g. pulp. On a percentage basis, depending on the magnitude of the sorption value, the confidence interval ranges from $\pm$ 3% for the high levels of PMG retention to $\pm$ 8% for the very low gum retention levels. The corresponding calculations for the data in Table X yielded a standard deviation of $\pm$ 3 x 10^{-4} g./g. pulp. This represents, at the 90% level of significance, a calculated confidence interval of $\pm$ 1.8 x 10^{-3} g./g. pulp. For these values on a percentage basis, the corresponding confidence interval range may extend $\pm$ 2 to 10%.

Further evidence of the reliability of the individual sorption measurements may be obtained by considering the reproducibility of the over-all sorption experiment. In Table X and plotted in Figure 2, Runs A and B represent duplicate sorption experiments performed at two different times on Pulp C-IV. The agreement between these completely independent experiments is excellent.

In view of the high precision of the PMG sorption measurements, and the excellent agreement between duplicate sorption runs, it was believed possible to reduce the PMG sorption analyses to individual determinations without sacrificing over-all reliability. Runs C and D in Table XI and Figure 3 represent the results of duplicate sorption experiments where a single determination was made of PMG retention.

It will be noted in Figure 3 that one smooth curve through the experimental points represents both sets of data. Any individual variation for each data point would tend to be smoothed out by the over-all sorption curve.

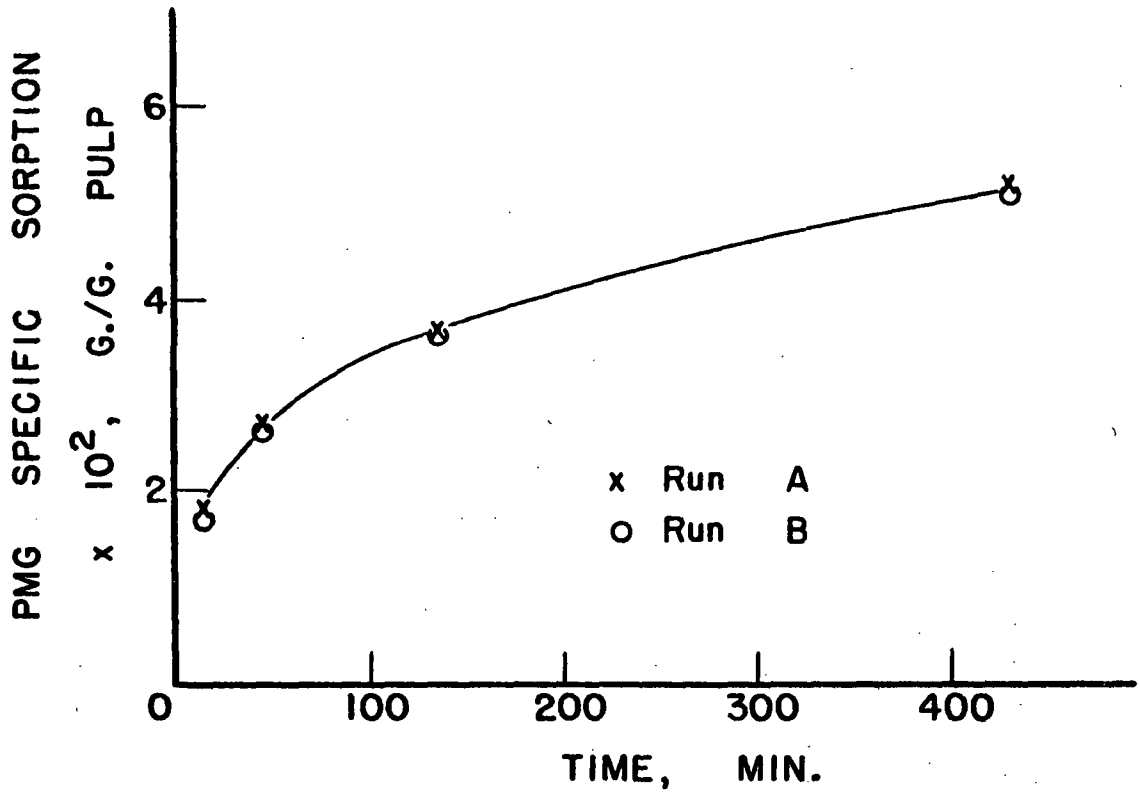

Figure 2. Reproducibility of PMG Sorption-Time Experiments

TABLE XI

REPRODUCIBILITY OF LBG SORPTION-TIME EXPERIMENTS

Pulp Fraction C-II, 11,780 sq. cm./g.
Pulp Consistency, 0.0167%
Temperature 25°C.
pH, 6.5

PMG Concn., g./l.	Time, sec.	PMG Specific Sorption x 10^3, g./g. pulp Run C	Run D
0.0125	30	0.898	0.771
	60	1.13	1.25
	120	1.84	1.88
	180	2.30	2.34
	300	2.80	2.82
	540	3.56	3.63
	780	4.36	4.45

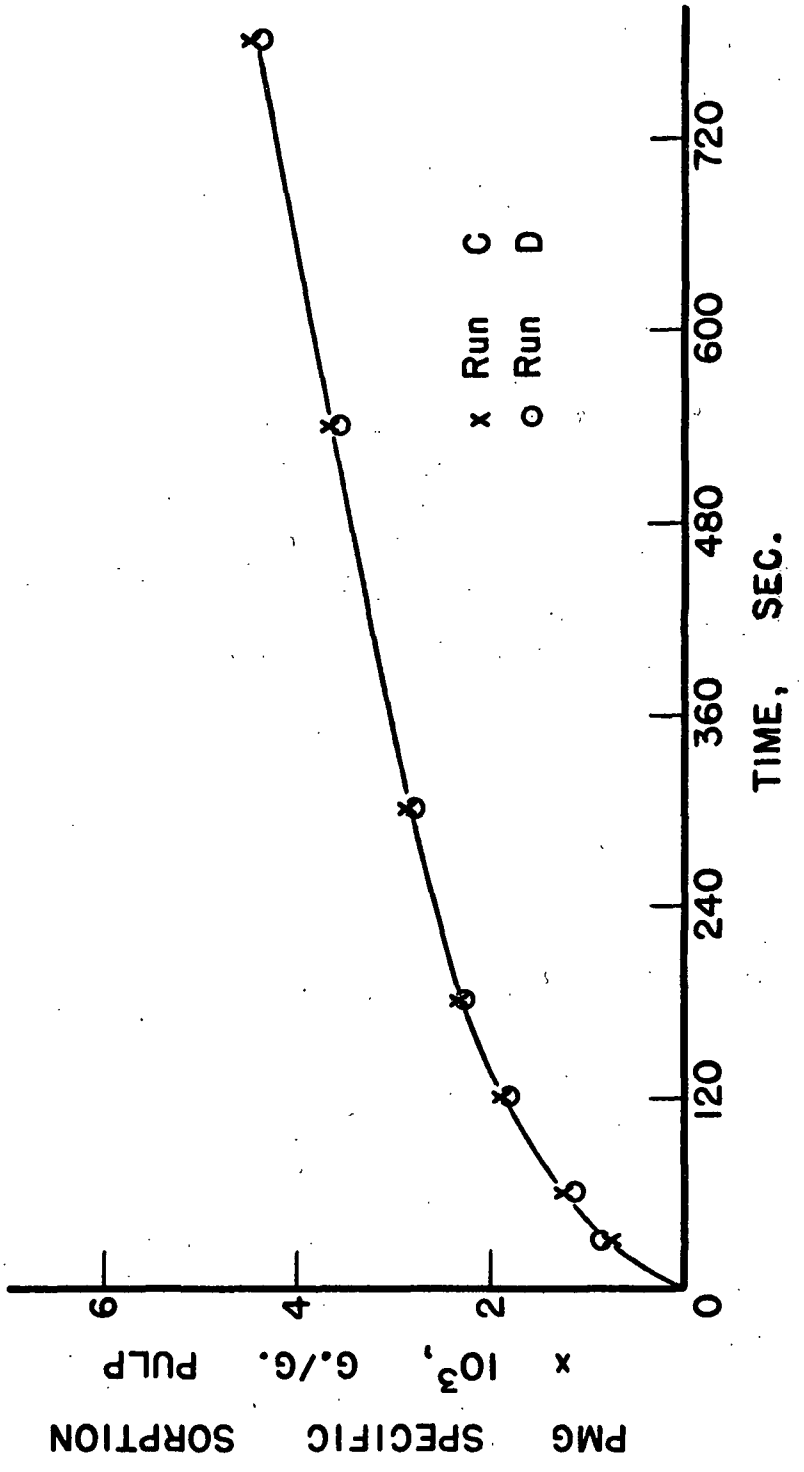

Figure 3. Reproducibility of PMG Sorption-Time Experiments

It was therefore concluded that single PMG sorption analyses at spaced time intervals were sufficiently reliable for the purposes of this study, and this procedure was used for all subsequent sorption experiments.

PRESENTATION AND DISCUSSION OF EXPERIMENTAL RESULTS

EFFECT OF TIME AND PMG CONCENTRATION ON SORPTION

The effect of time on the sorption of PMG was investigated using Pulp C-II, and initial PMG concentrations ranging from 0.005 to 0.100 g./l. The pulp consistency was 0.0167% at a pH of 6.5. These sorption runs were conducted at 25 $\pm$ 0.2°C. The results of these experiments are presented in Table XII and are plotted in Figure 4.

In a heterogeneous system such as this, it has been pointed out that both physical transport and chemical kinetic steps may be involved in the over-all sorption phenomenon. Many times an insight into the rate-determining factors in such a system may be obtained from knowledge of the functional dependence between the initial rate and concentration.

For the PMG sorption curves in Figure 4, analytical rate expressions may be determined; however, at time equal to zero, these relationships are indeterminate. It was therefore necessary to evaluate the initial rate graphically. The technique employed was that described by Livingston (28). A plane mirror tangentimeter was used to determine the slope, at zero time, of the curves in Figure 4. These data are presented in Table XIII.

TABLE XII

EFFECT OF TIME AND CONCENTRATION ON PMG SORPTION

Pulp Fraction C-II, 11,780 sq.cm./g.
Pulp Consistency, 0.0167%
Temperature, 25°C.
pH, 6.5

Initial PMG Concn., g./l.	Time, sec.	PMG Specific Sorption x 10^3, g./g. pulp	Calculated Residual PMG Concn., g./l.	Decrease in PMG Concn., %
0.100[a]	60	4.38	0.0993	0.7
	120	5.83	0.0990	1.0
	200	7.22	0.0988	1.2
	300	8.38	0.0986	1.4
	900	12.34	0.0979	2.0
0.050[a]	60	3.10	0.0494	1.2
	120	4.37	0.0493	1.4
	180	4.89	0.0492	1.6
	300	5.88	0.0490	2.0
	600	7.53	0.0487	2.6
	900	9.42	0.0484	3.2
0.025[a]	40	1.15	0.0248	0.8
	60	1.75	0.0247	1.2
	120	2.67	0.0246	1.6
	180	3.13	0.0245	2.0
	300	3.87	0.0244	2.4
	540	5.20	0.0241	3.6
	780	5.88	0.0240	4.0
0.0125[c]	30	0.834	0.01236	1.1
	60	1.18	0.01230	1.6
	120	1.86	0.01219	2.5
	180	2.32	0.01211	3.1
	300	2.81	0.01203	3.7
	540	3.60	0.0119	4.8
	780	4.40	0.0118	5.6
0.005[b]	30	0.610	0.00490	2.0
	60	0.669	0.00489	2.2
	120	1.05	0.00482	3.6
	180	1.35	0.00478	4.4
	300	1.63	0.00473	5.4
	540	2.21	0.00463	7.4
	780	2.71	0.00460	8.0

[a] PMG specific sorption -- average of duplicate analyses, single run.
[b] PMG specific sorption -- single analysis, single run.
[c] PMG specific sorption -- average of duplicate sorption run, single analysis.

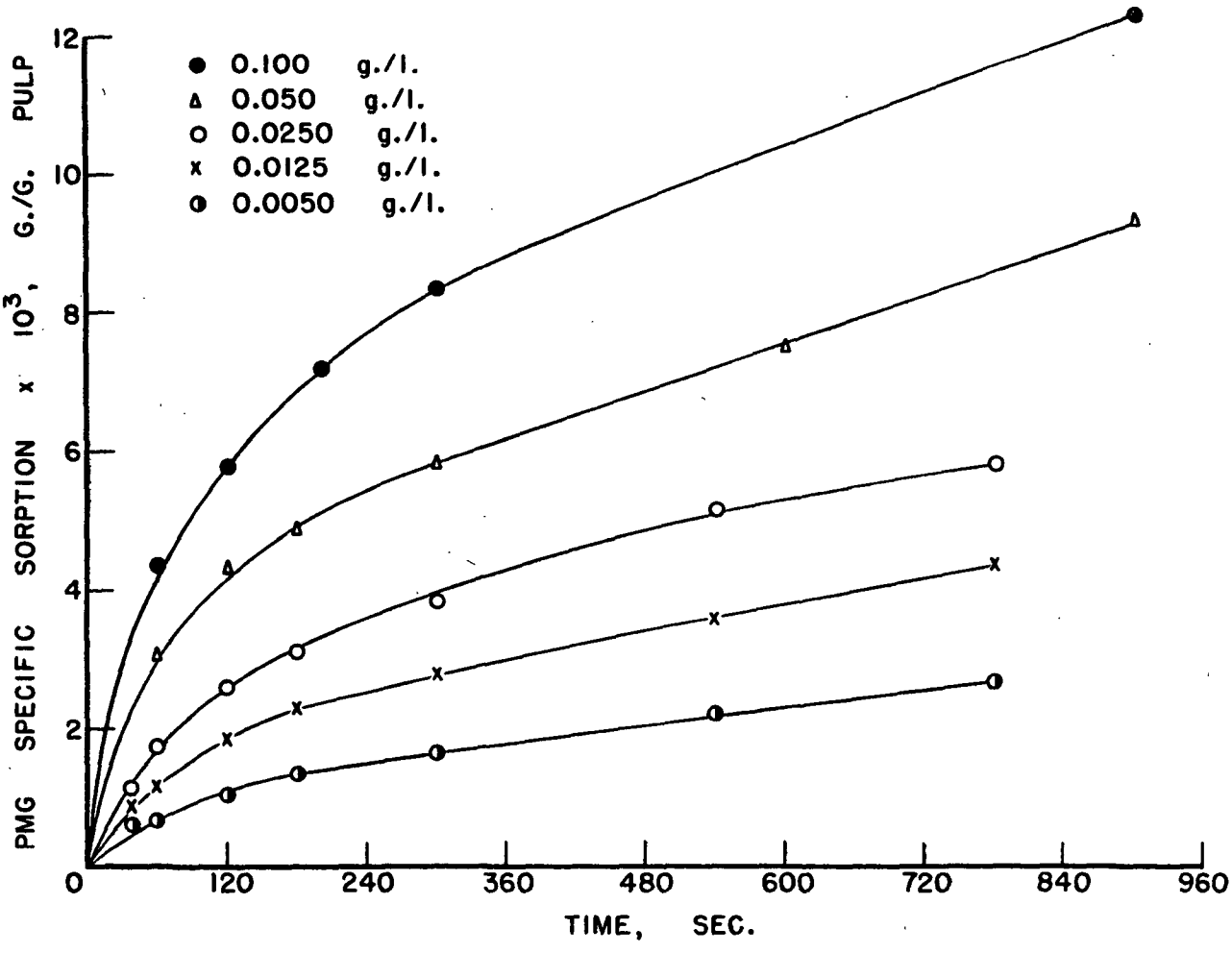

Figure 4. Effect of Time and Concentration on PMG Sorption

TABLE XIII

RELATIONSHIP BETWEEN INITIAL RATE OF PMG SORPTION AND INITIAL PMG CONCENTRATION

Initial PMG Concn., g./l.	Initial Rate of PMG Sorption x 10^5, g./g. pulp per sec.
0.005	2.7
0.0125	4.5
0.0250	7.2
0.050	11.8
0.100	16.1

From the data of Table XIII, Figure 5 was constructed, describing the relationship between initial rate of PMG sorption and initial PMG concentration. It may be noted that increased initial PMG concentrations resulted in an increase in initial sorption rate.

The initial rate of sorption was found empirically to fit the equation

$$\underline{R_o} = \underline{k}\underline{c}^{0.61} \qquad (1)$$

where $\underline{R_o}$ = over-all initial PMG sorption rate, g./g. pulp per second.

$\underline{c}$ = initial PMG concentration, g./1000 g.

$\underline{k}$ = constant, $sec.^{-1}$

In Equation (1) above, "$\underline{k}$" should not be construed as a true reaction rate constant for it may contain hidden components. Daniels (29) has pointed out the dangers of inadequate consideration of all the factors involved in studies of rate processes. All too often data are forced to

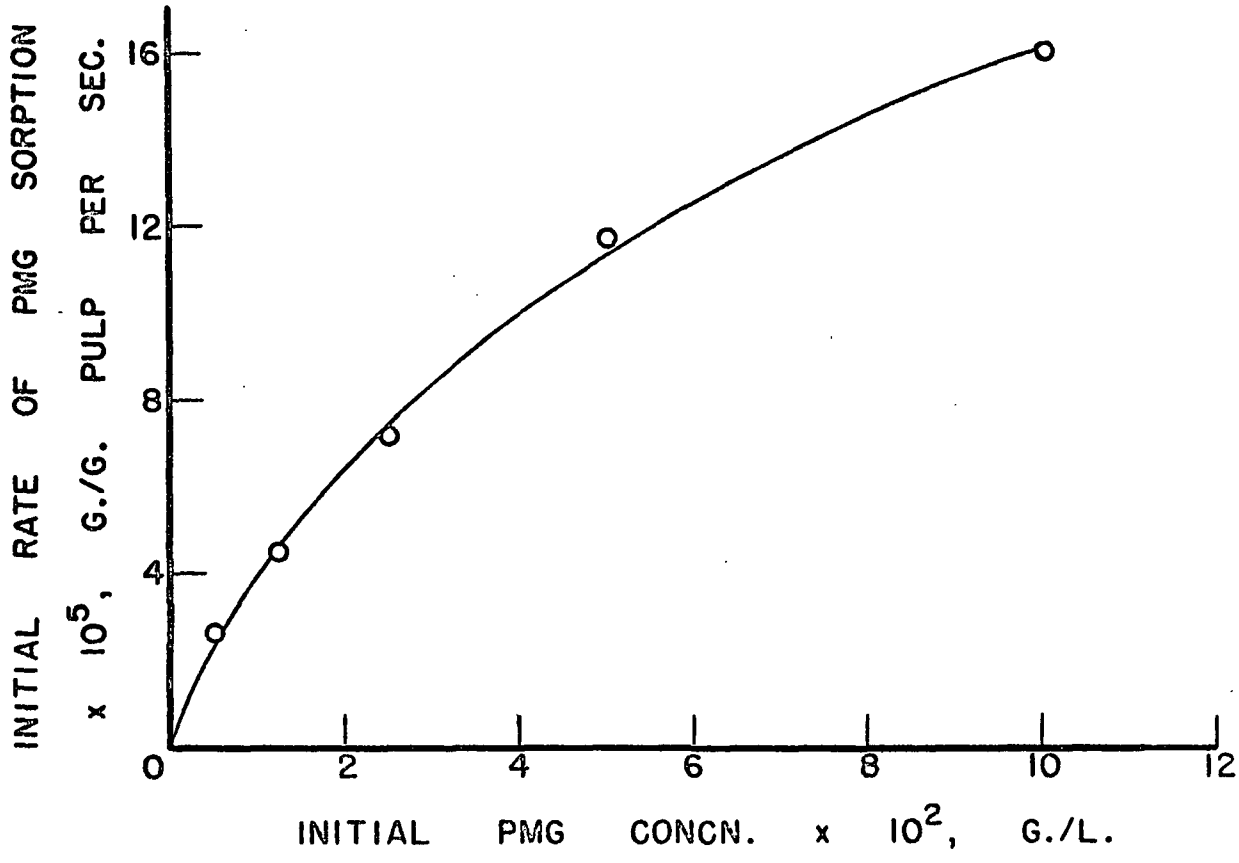

Figure 5. Relationship Between Initial Rate of PMG Sorption and Initial PMG Concentration

fit simple relationships where a more complex situation exists. Both diffusional and chemical kinetic effects may be involved in the empirical constant, "k". Here, as is explained later in this thesis, "k" is affected by the degree of agitation in the system.

Any hypothesis of the rate-determining factors involved in PMG sorption would have to be consistent with the functional dependence on concentration, as described in Equation (1). In rate studies, this analysis is normally aided by the criterion of the order of reaction. Here, the fractional exponent of the concentration term indicates a complex reaction. Little distinction can be made between the effect of a diffusional transport step or the possibility of a complex adsorption reaction on the over-all initial rate process. Both of these phenomena may be interpreted as consistent with the rate equation noted above.

For a sorption mechanism dependent on a diffusional transport step, the functional dependence on concentration may be either of the first or some fractional order. Where the coefficient of diffusion is a constant, a first order relationship would result in accord with Fick's law. For a diffusional process in which the diffusion coefficient depended on concentration, a fractional reaction order could be obtained. In polymer systems this behavior is not unusual (30, 31, 32).

Similarly, for an adsorption process, a fractional order with respect to concentration is also possible. For example, Langmuir (33) points out that the order of such reactions may be zero, first, second, or some intermediate value.

In summary, the experimentally observed functional dependence expressed in Equation (1), between the rate of PMG sorption and concentration, presents an important limiting condition. This is one of the elements which must be met in any ultimate test of a proposed mechanism for the rate processes in this system.

EFFECT OF TEMPERATURE ON SORPTION

The variation of reaction velocity with temperature is a most powerful criterion for assessing the mechanism of any rate process. High temperature coefficients for a reaction usually indicate a chemical process; while, in contrast, a low temperature coefficient suggests a physical process, such as diffusion or adsorption of the van der Waals type.

Using an initial PMG concentration of 0.0125 g./l., and Pulp C-II, the effect of temperature in PMG sorption was studied. As in the previous sorption experiments, an infinite bath was approximated by working at a pulp consistency of 0.0167%. The sorption data are given in Table XIV and are plotted in Figure 6.

The desired temperature dependence of the initial rate of PMG sorption was calculated from the sorption curves in Figure 6. These data are presented in Table XV are are plotted in Figure 7. For a 10°C. rise in temperature, the calculated average temperature coefficient is 1.3, which is consistent with a diffusional transport step as rate-controlling in the over-all sorption phenomenon. A temperature coefficient of 1.3 is reported, for example, by Zimmerman (34) for diffusional processes in

TABLE XIV

EFFECT OF TEMPERATURE ON PMG SPECIFIC SORPTION

Pulp C-II, 11,780 sq.cm./g.
Pulp Consistency, 0.0167%
Initial PMG Concn., 0.0125 g./l.
pH, 6.5

Temperature, °C.	Time, sec.	PMG Specific Sorption x 10^3, g./g. pulp
5	38	0.483
	75	0.706
	128	1.11
	300	1.63
	555	2.47
	790	3.03
25	30	0.834
	60	1.18
	120	1.86
	180	2.32
	300	2.81
	540	3.60
	780	5.80
45	30	1.08
	60	1.62
	120	2.49
	180	3.05
	300	3.71
	540	4.96
	780	5.80
61	60	2.28
	120	2.85
	180	3.70
	300	4.72
	540	6.14
	780	7.00

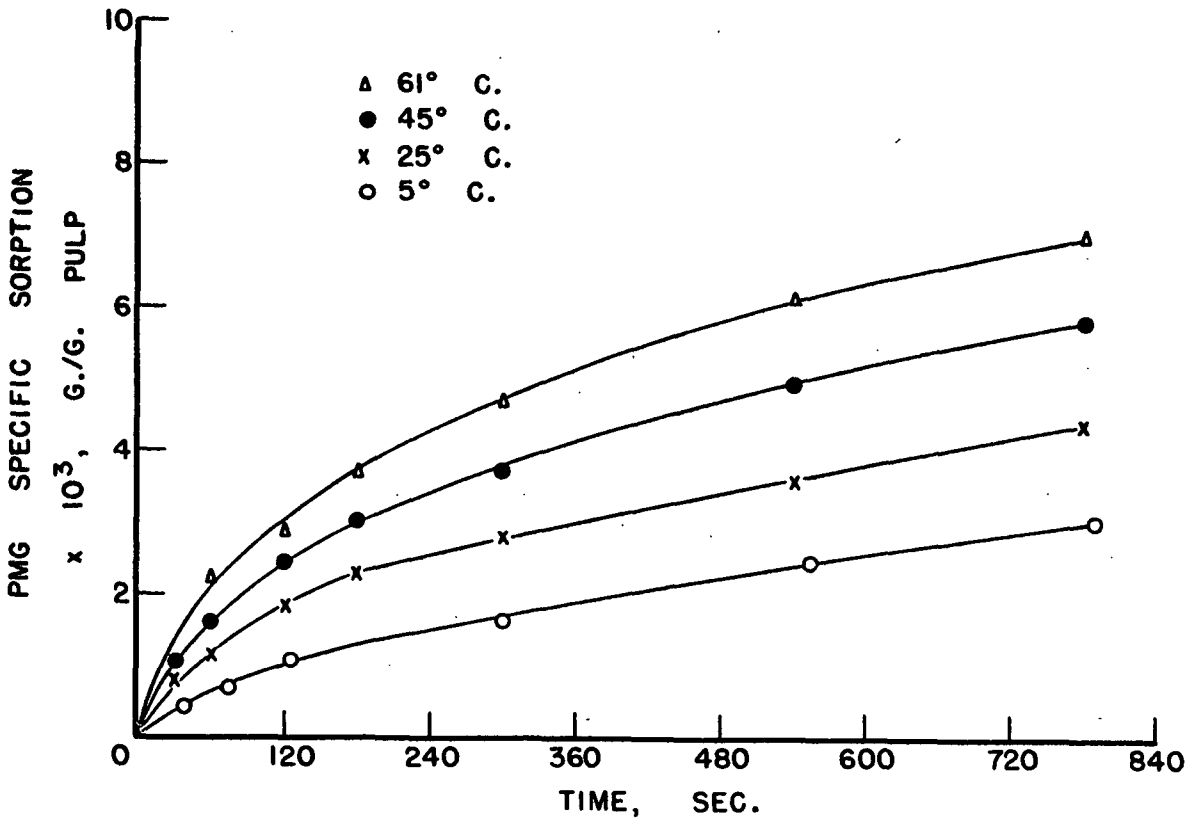

Figure 6. Effect of Temperature on PMG Sorption

aqueous systems. This is in contrast with a chemical reaction which generally involves high energies of activation, and in which the temperature coefficient for a 10°C. rise in temperature may range from 2 to 4.

TABLE XV

RELATIONSHIP BETWEEN INITIAL RATE PMG SORPTION AND TEMPERATURE

Temperature, °C.	Initial Rate PMG Sorption x 10^5, g./g. pulp per sec.
5	2.67
25	4.50
45	7.33
61	10.35

In addition to considering the temperature coefficient of the initial rate of PMG sorption, it is perhaps even more fruitful to consider the energy of activation for sorption derived from this temperature coefficient. Whether one considers the effect of temperature on sorption rate from the standpoint of absolute reaction rate theory, or the originally empirical relationship of Arrhenius, the variation in the rate constant may be expressed as (35),

$$\underline{k} = \underline{s}e^{-\Delta \underline{E}_a/\underline{RT}} \qquad (2)$$

where $\underline{k}$ = reaction rate constant

$\underline{s}$ = constant

$\Delta \underline{E}_a$ = energy of activation

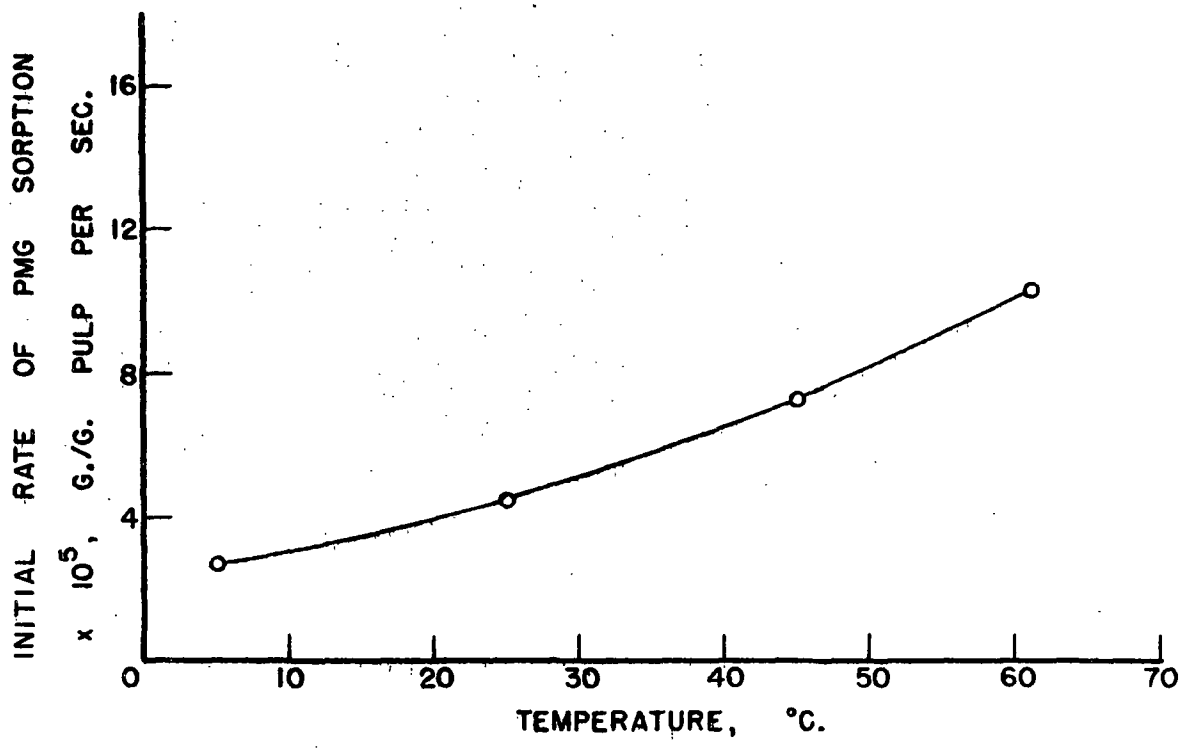

Figure 7. Relationship Between Initial Rate of PMG Sorption and Temperature

R = gas constant

T = absolute temperature

This equation may be said to be perfectly general, applying to both chemical reactions and physical changes.

Set in logarithmic form, Equation (2) may be expressed as

$$\ln k = -\Delta Ea/RT + \ln s \qquad (3)$$

According to Equation (3) a straight line is produced when $\ln k$ is plotted against the reciprocal of absolute temperature. The slope of such a line equals $-\Delta Ea/RT$ from which the energy of activation, ΔEa, may be evaluated.

Inasmuch as the specific or true reaction rate constant is an unknown for the PMG-pulp system under study, as has been previously discussed, it is convenient to calculate the energy of activation from initial rate-temperature data. The modified equation would be of the same form as in Equation (3), but with the initial rate, R_o, substituted for the reaction rate constant, k, a concentration term appears in the intercept.

$$\ln R_o = \frac{-\Delta Ra}{RT} + \ln s + 0.61 \ln c \qquad (4)$$

Figure 8 is a plot of equation (4) based on the data found in Table XV. In Figure 8, the base of the logarithm has been converted from the Napierian to the Briggsian system. From the slope of the line an activation energy of 4400 cal./mole was calculated. The "mole" in the

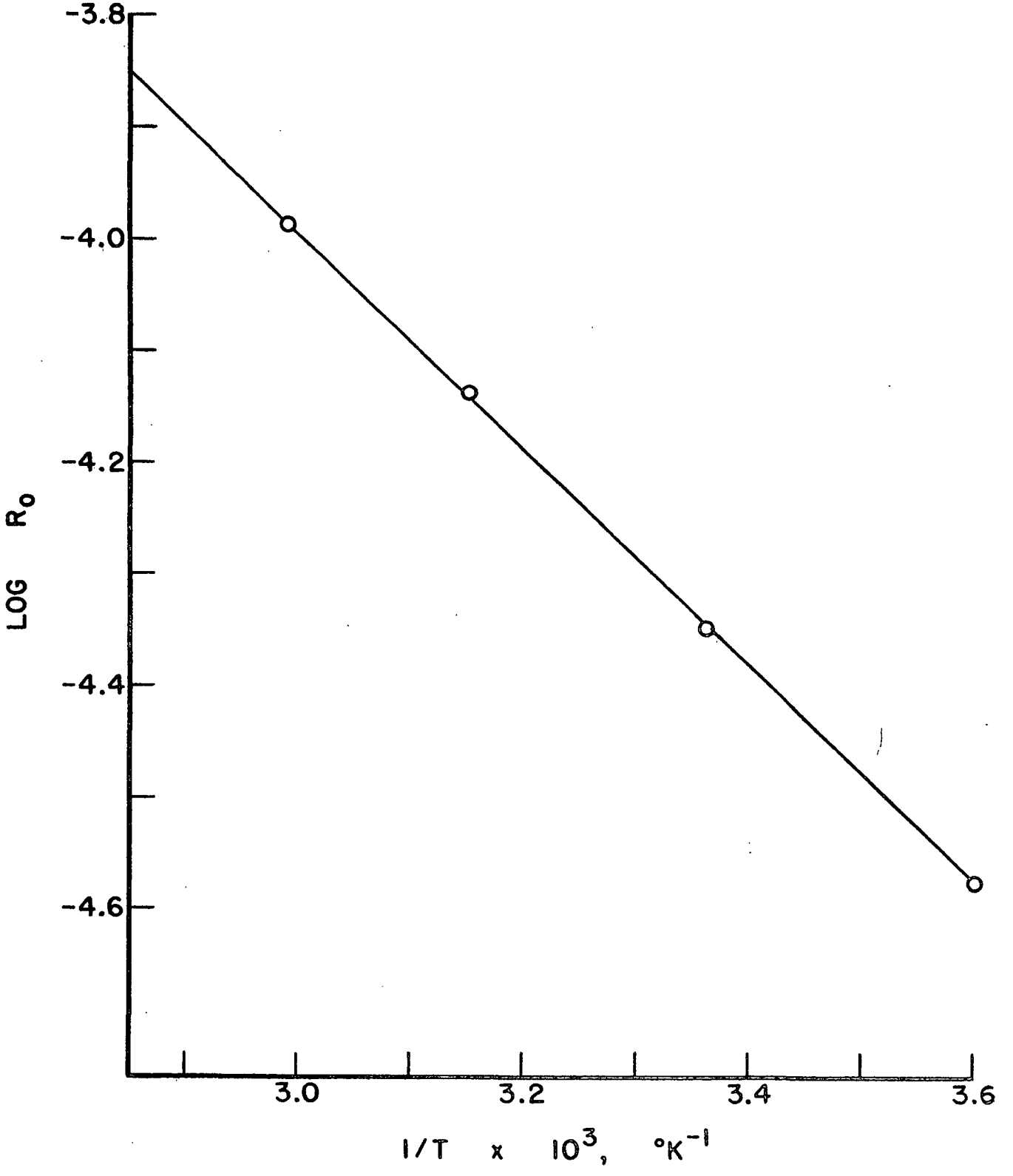

Figure 8. Initial Rate of Sorption Data in Form of Arrhenius Equation for Calculation of Activation Energy

expression for the energy of activation refers to the kinetic unit involved in the rate process. For a physical diffusion process, this reference is made to the solvent; for a chemical reaction or sorption process involving a polymer, this unit cannot be unequivocally defined at this time. In such cases, the "mole" or kinetic unit is usually considered in terms of the reactive segment of the polymer chain.

It may be recalled that the energy of activation represents the critical increase in energy required by the constituent molecules of a system prior to their participation in a chemical or physical process. As such, the determination of activation energies has proven to be a valuable aid in the investigation of reaction mechanisms. In many kinetic studies, a consideration of the order of magnitude of the energy of activation provides an insight into the nature of the phenomenon. For example, the range of activation energies for ordinary measurable chemical reactions is of the order of 15 to 60 kcal./mole (35). Similarly, chemisorption or "activated adsorption" involves relatively high energies of activation, frequently of the order of 20 kcal. (36). In contrast, physical processes, such as the flow of a liquid, diffusion in solution, or van der Waals type adsorption, require very little activation energy. The processes of viscous flow and diffusion are quite similar, and for normal liquids involve energies of activation of about 3 to 5 kcal./mole (37). For adsorption of the van der Waals type which is generally accompanied by small heat changes, of the order of 5 kcal. or less, little consideration is given to an energy of activation (37-39), the implication being that it is no larger than the magnitude of the heat changes.

In the present research, the calculated energy of activation, 4400 cal./mole, is most significant. The order of magnitude of this value is indicative of a physical process as rate determining in the over-all PMG sorption phenomenon. A diffusional transport step, adsorption of the physical or van der Waals type, or a combination of both these processes may be involved. Here, chemisorption or a chemical reaction of PMG at the fiber surface are improbable as initial rate determining, since such phenomena would involve much greater activation energies, as has been pointed out above.

EFFECT OF AGITATION ON SORPTION

The logical deduction from the observed experimental results of the temperature study is that a physical process is the important rate-controlling factor in the over-all sorption of PMG. It is suggested that such a process may involve a diffusional transport step, or physical adsorption of the van der Waals type. In the following experiments, the importance of a diffusional transport step was investigated further by studying the effect of agitation on the sorption of PMG. If a physical transport step is important in the PMG-pulp system, then the agitation action, by reducing the resistance to molecular transfer, should result in an increased sorption of gum.

The experiments designed to test the validity of a physical transport hypothesis were conducted on Pulp C-II at an initial PMG concentration of 0.0125 g./l. The pulp consistency was 0.0167%, and the temperature maintained at 25°C. throughout the sorption runs. These sorption

studies were conducted in a standard British Pulp Disintegrator modified to operate at 3000, 2120, and 1500 r.p.m.

In these experiments it was necessary to consider the effect of agitation on the pulp itself. Ingmanson (40) has demonstrated that the hydrodynamic specific surface area of pulp fibers increases with stirring in a British Disintegrator. In addition, other concomitant changes occur; for example, the imbibition of water increases as reflected in the specific volume, and fiber flexibility is affected.

Provision was made in the experimental design for correcting the sorption data for the effect of agitation on the pulp. The increased PMG sorption resulting from modification of the pulp fibers was assessed by means of control runs. These controls consisted of parallel standard PMG sorption runs, made on two series of pulp samples. In one series, prior to the sorption run, the pulp was subjected to agitation in a British Disintegrator at 3000 r.p.m. for 780 seconds. Such conditions of preagitation represent the most extreme action the pulp fibers will be subjected to in the subsequent agitation experiments. In the other series there was no preliminary treatment to the pulp fibers. Any difference in PMG retention between these runs represents the effect of agitation on the pulp itself. The sorption data are presented in Table XVI and are plotted in Figure 9.

From the data of Table XVI and the curves in Figure 9, it may be noted that the amount and rate of PMG sorption increased markedly with increasing agitation. The portion of the increased sorption which may be

TABLE XVI

EFFECT OF AGITATION ON PMG SPECIFIC SORPTION

Pulp C-II, 11,780 sq.cm./g.
Pulp Consistency, 0.0167%
Initial PMG Concn., 0.0125 g./l.
Temperature, 25°C.
pH, 6.5

Time, sec.	PMG Specific Sorption x 10^3, g./g. pulp				
	Control Runs		Degree of Agitation, r.p.m.		
	Standard Run [a]	Preagitated Samples [b]	1500	2120	3000
30	0.77	0.81	----	----	----
60	1.20	1.26	1.38	1.50	1.62
120	1.78	1.94	2.11	2.29	2.47
240	----	2.76	2.95	3.18	----
300	2.84	3.09	3.34	3.58	3.88
500	3.72	4.03	4.37	4.61	5.07
780	4.60	5.06	5.41	5.83	6.28

[a] Standard procedure for sorption runs. Used throughout experimental program, tumbling at 12 r.p.m.
[b] Pulp samples agitated in British Disintegrator at 3000 r.p.m. for 780 sec. prior to standard sorption run as described above.

attributed to the modification of the pulp fibers, resulting from agitation, was small. In the most extreme case, at 780 seconds, the increase due to this factor amounted to 10%, and at the 60-second interval it was but 5%. At 3000 r.p.m., the sorption was as much as 35% greater than that of the reference control run. To obtain a comparable increase by

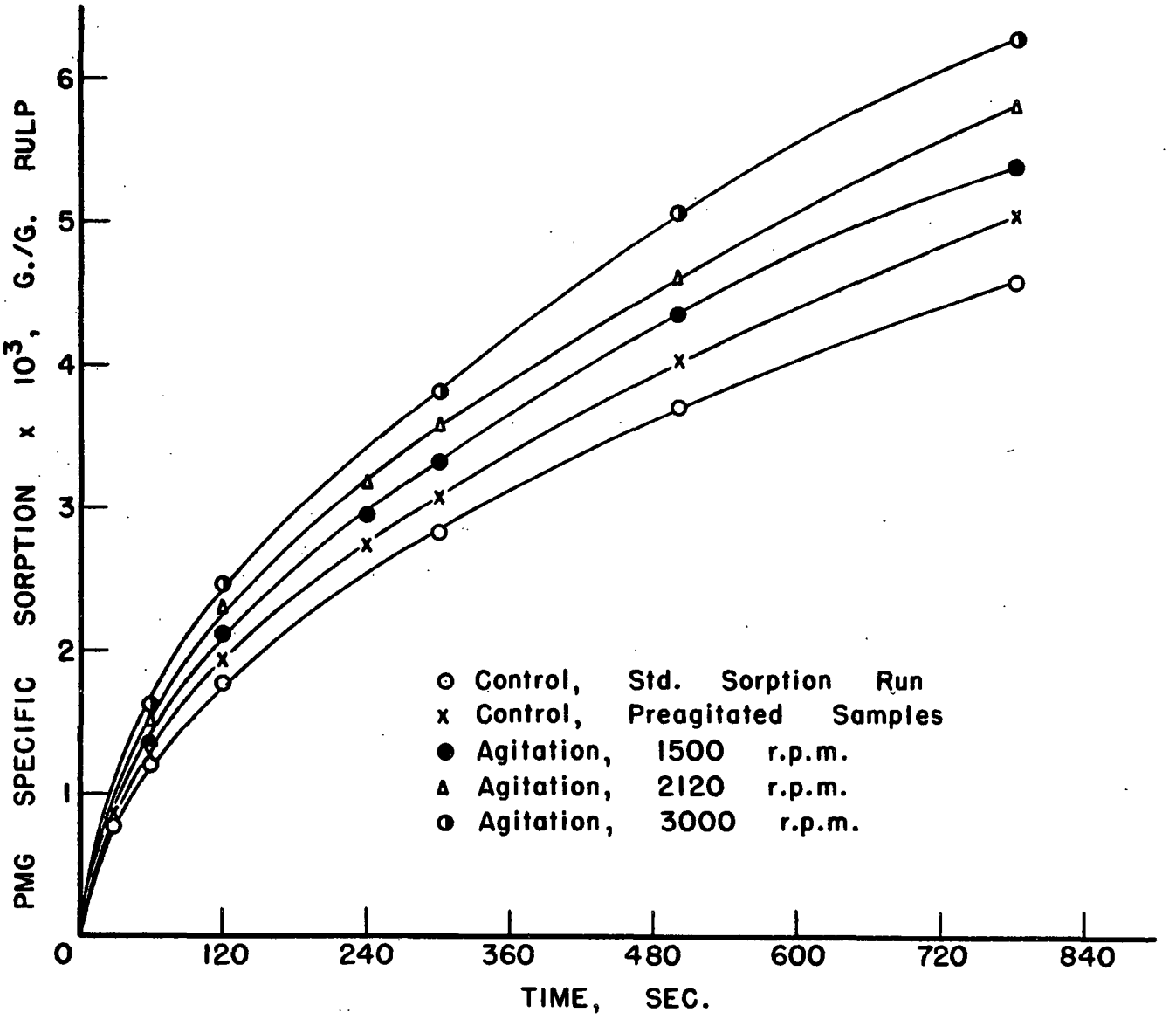

Figure 9. Effect of Agitation on PMG Specific Sorption

varying the PMG concentration, it would have been necessary to approximately double the initial concentration.

The initial rates of PMG sorption, for the three conditions of agitation, were calculated from the curves in Figure 9 as previously described, and are presented in Table XVII. These data are corrected for the effect of agitation on the pulp itself by reference to the control run. A linear correction was applied for the sorption runs at 2120 and 1500 r.p.m., based on the control data at 3000 r.p.m. The calculated initial rates of PMG sorption were not corrected for the slight additional increase in specific surface which may have resulted from the gum being present during the agitation. Although an apparent peptizing effect of this nature has been suggested for some related systems, it is felt that in connection with initial rate studies the influence of such an effect is sufficiently small to be considered negligible. The dependence of the initial rate of PMG sorption on the degree of agitation is shown graphically in Figure 10.

The marked dependence of PMG sorption on the degree of agitation is a most important experimental observation. It confirms the hypothesis that in the PMG-pulp system, a transport process represents an important rate-determining step in the over-all sorption phenomenon. If a transport step were not important, the observed PMG sorption would have been uninfluenced by the stirring or agitation action.

The exact nature of this transport phenomenon cannot be completely described at this time. Under the conditions of agitation used in this

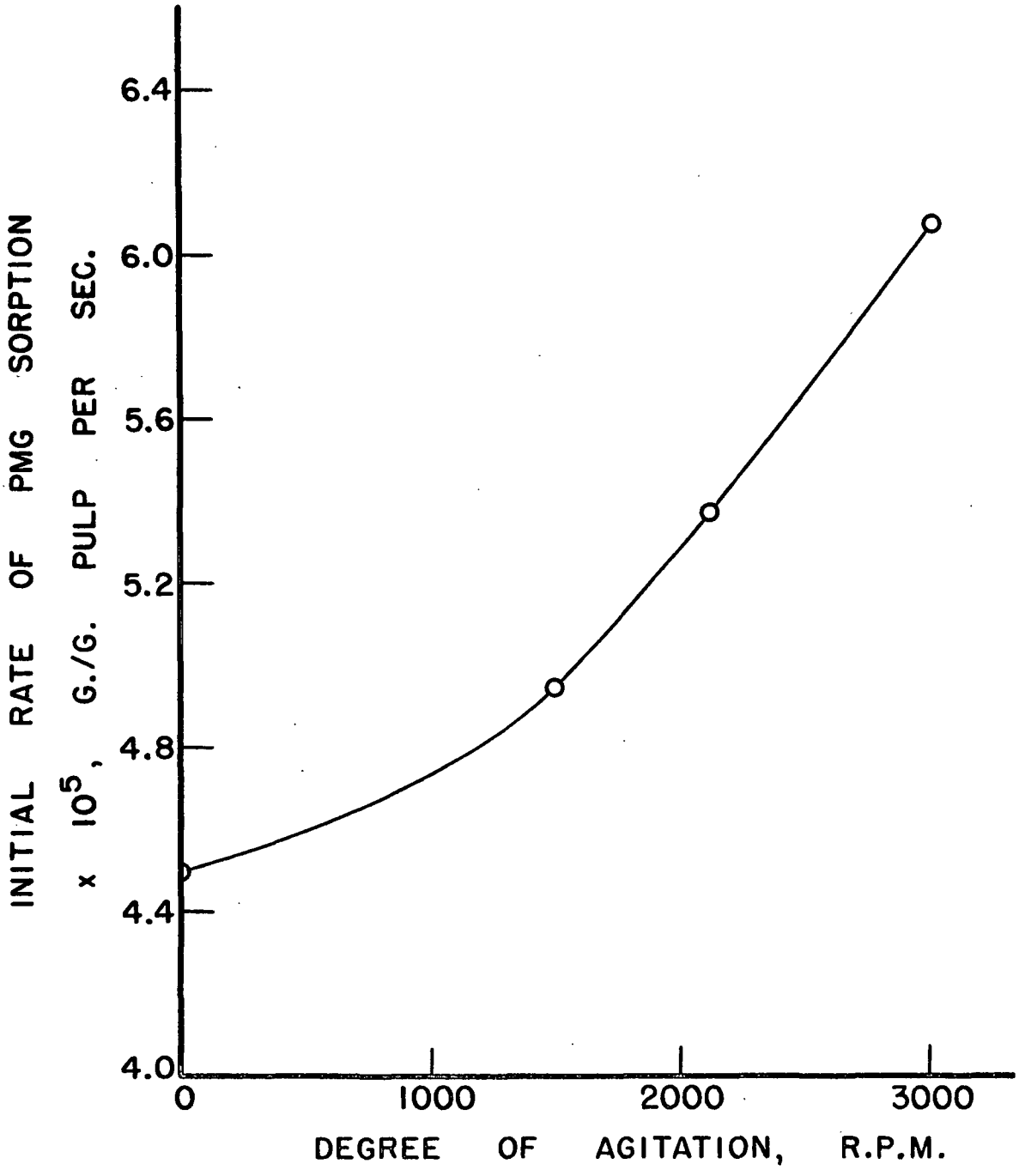

Figure 10. Relationship Between Initial Rate of PMG Sorption and Degree of Agitation

TABLE XVII

RELATIONSHIP BETWEEN DEGREE OF AGITATION AND THE INITIAL RATE OF PMG SORPTION

Degree of Agitation, r.p.m.	Initial Rate of PMG Sorption x 10^5, g./g. pulp per sec.	Increase in Sorption With Agitation, %
Standard Procedure Control, 12 r.p.m.	4.50	----
1500	4.95	11.0
2120	5.38	19.5
3000	6.08	35.0

research, bulk diffusion would not be expected to be a factor of importance. It will be recalled that a tumbling action provided for the constant mixing of the PMG-pulp system throughout the sorption experiments. However, while providing for mixing in the PMG-pulp suspension, this tumbling action was mild, and it may be postulated that a resistance to the transfer of PMG existed at the fiber-liquid interface. Conceivably, this resistance may be present as a stagnant film of liquid from the bulk phase, or as loosely held layers of imbibed water associated with both the fiber and the gum.

It is suggested that the tangential shearing stresses accompanying stirring reduces these resistances, and thus enhances the transfer of PMG to the fiber surface. Such an analysis is consistent with a consideration of Fick's first law of diffusion. From Fick's law an inverse relationship exists between the rate of diffusion and the equivalent resistance to

molecular transfer. Thus, a decrease in the equivalent film thickness would manifest itself in an increased rate of molecular transport as was observed here.

EFFECT OF PULP SPECIFIC SURFACE ON SORPTION

In approaching the present study of PMG sorption, a transport process and adsorption proper at the fiber surface were suggested as process steps in the over-all sorption phenomenon. For both these steps, the area involved in the process is an important variable. As such, it is interesting to consider the dependence of PMG sorption on the "surface area" of pulp fibers.

Classically, a diffusional transport process bears a direct relationship with area. On the other hand, for many adsorption processes, the dependence on area cannot be expressed as succinctly because of the complexities of the surfaces involved. For pulp fibers, as with many materials, "surface area" is difficult to define and consequently is often described in terms of the method of evaluation. Here, hydrodynamic specific surface area from filtration resistance measurements was taken as a measure of the "surface area" of the pulp fibers.

The effect on PMG sorption of an increase in pulp hydrodynamic specific surface area, as developed by beating, was investigated at one level of PMG concentration and one temperature. The initial PMG concentration was 0.100 g./l., the temperature 25°C., and the consistency maintained at 0.0167%. The sorption-time data for pulps having hydrodynamic specific

surface areas of 9260, 11,780, 15,610, and 29,900 sq.cm./g. are presented in Table XVIII and plotted in Figure 11.

TABLE XVIII

EFFECT OF PULP SPECIFIC SURFACE ON PMG SORPTION

Pulp Consistency, 0.0167%
Temperature, 25°C.
Initial PMG Concn., 0.10 g./l.
pH, 6.5

Pulp Specific Surface, sq.cm./g.	Time, sec.	PMG Specific Sorption x 10^3, g./g. pulp
9260	30	2.27
	60	3.37
	120	4.53
	180	5.64
	300	6.66
	540	8.59
	780	10.10
11,780	60	4.38
	120	5.83
	200	7.22
	300	8.38
	900	12.34
15,610	60	4.71
	120	6.04
	180	7.45
	300	9.10
	780	13.25
29,900	60	6.78
	120	9.21
	240	11.80
	480	13.80
	900	17.20

As one would expect, the amount and rate of PMG sorption increased with increasing specific surface. The effect of specific surface on the

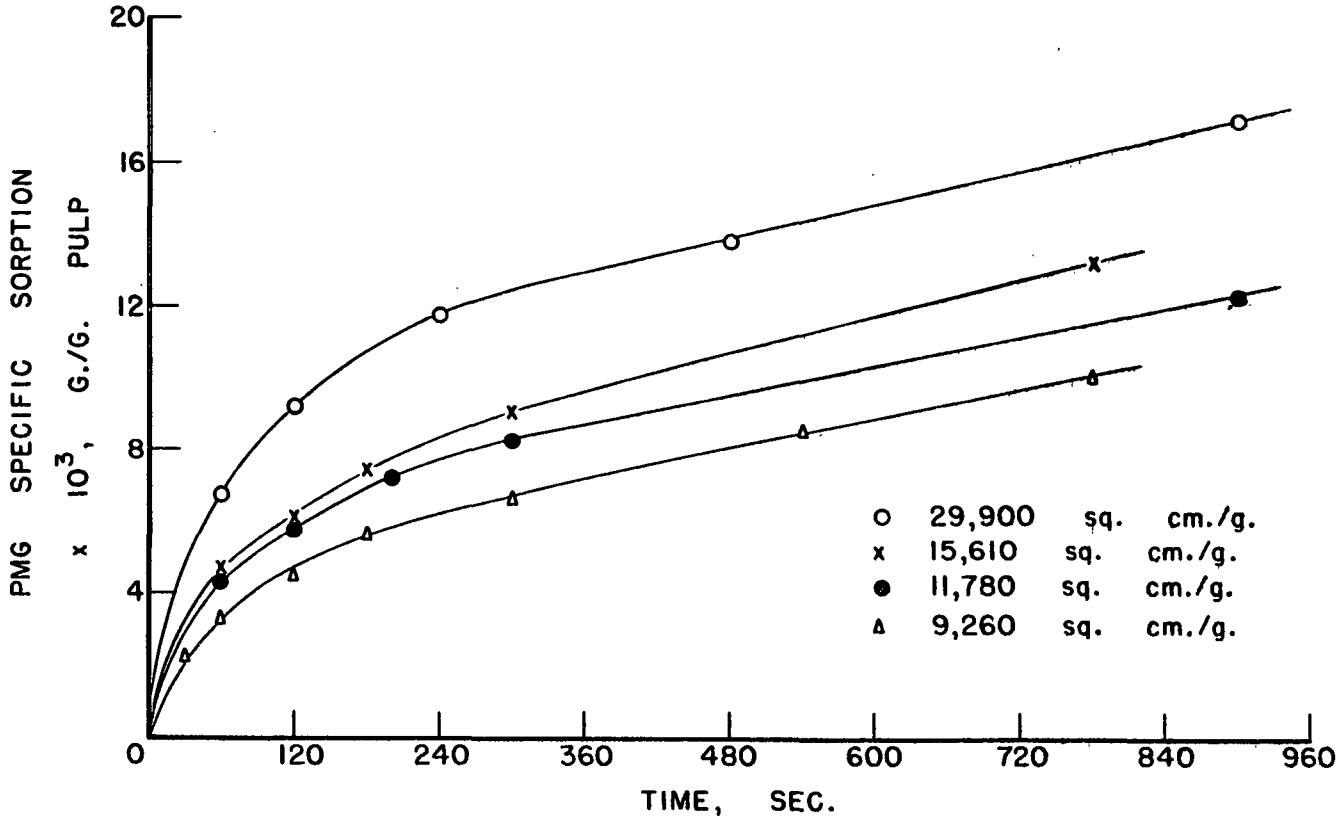

Figure 11. Effect of Pulp Specific Surface on PMG Sorption

initial rate of PMG sorption was calculated from the curves in Figure 11, as previously described, and is presented in Table XIX. These data are plotted in Figure 12.

TABLE XIX

RELATIONSHIP BETWEEN INITIAL RATE OF PMG SORPTION AND PULP SPECIFIC SURFACE

Pulp Specific Surface, sq.cm./g.	Initial Rate of PMG Sorption x 10^5, g./g. pulp per sec.
9260	14.8
11,780	16.1
15,610	17.9
29,900	26.5

A linear relationship is observed in Figure 12 between the initial rate of PMG sorption and hydrodynamic specific surface area. In view of the concomitant changes which occurred to the pulp with beating, this behavior is especially interesting. From this relationship it may be noted that the rate of change of PMG sorption with respect to hydrodynamic specific surface area is a constant, irrespective of other modifications to the pulp fiber. These data would indicate that the calculated hydrodynamic specific surface area bears some direct relationship to the actual surface involved in the over-all sorption phenomenon.

With beating, the development of surface area is not the only factor of importance in the sorption of PMG. The data demonstrate that the

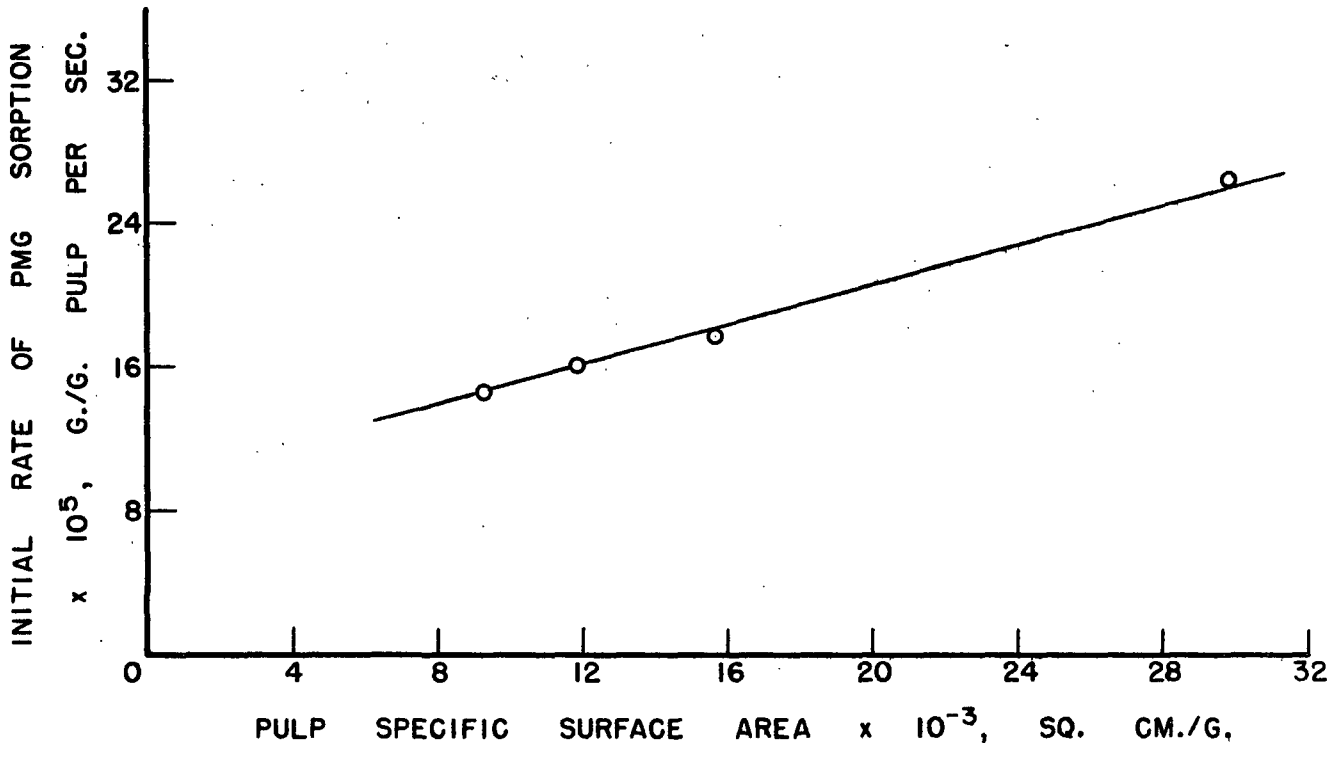

Figure 12. Relationship Between Initial Rate of PMG Sorption and Pulp Specific Surface

nature of the surfaces studied here were not identical with respect to the sorption of PMG. For example, at different levels of area development, a given increase in area does not produce equivalent changes in the rate of PMG sorption. A question of accessibility could be involved. Some of the external area developed by beating may be available to water flow in the hydrodynamic specific surface measurement, but not accessible for PMG sorption. On the other hand, a diffusion process may be of importance. Consistent with the basic hypothesis presented in this thesis, it is possible that the barrier presenting resistance to transport of PMG molecules is increased by changes in the fiber which occur on beating.

INTERPRETATION OF SORPTION EXPERIMENTS

The sorption studies of this research contribute to our basic understanding of the heterogeneous PMG-pulp fiber system. They provide an insight into the rate-determining factors in the sorption of PMG. Further, these studies make possible a hypothesized characterization of the sorption process itself.

THE FACTORS AFFECTING THE INITIAL RATE OF PMG SORPTION

From an analysis of the PMG-pulp system, two steps have been suggested as the important rate-determining factors in the over-all sorption phenomenon. These are first, a transport process, and second, adsorption proper at the fiber surface. The experimental results of each of the sorption studies have been discussed in view of these considerations.

The empirical relationship observed for the initial rate of PMG sorption as a function of concentration, was kinetically speaking, of a fractional order. Unfortunately, as has been previously discussed, both a diffusional transport process, or adsorption proper are consistent with this functional dependence on concentration. While no distinction between these processes is possible here, this observation establishes an important limiting condition. It is one of the elements which must be met in evaluating a proposed mechanism for the rate processes in this system.

Of much greater significance is the observed temperature dependence of the initial rate of sorption. For each 10°C. rise in temperature, the initial rate of sorption was increased by a factor of 1.3; the magnitude

of this temperature coefficient is consistent with a diffusional transport step as rate-controlling in the over-all PMG sorption phenomenon. The importance of a physical rate-determining process was elaborated by the calculated energy of activation for the initial rate of PMG sorption. The figure of 4400 cal./mole is strongly suggestive of a diffusional transport process, adsorption of the van der Waals type, or a combination of both these processes as rate-determining. Since the value 4400 cal./mole reflects the rate-determining step in the over-all process, the adsorption step per se cannot require a greater energy of activation. Consequently, the possibility of a high energy, slow chemisorption step is excluded. The adsorption proper at the liquid-solid interface must therefore be of the physical or van der Waals type, and would be expected to be quite rapid. Thus, adsorption alone cannot be expected to be rate-determining. From this analysis, the adsorption step must occur at a rate in excess of or comparable in magnitude to that of the transport process.

The observed results of the agitation experiments further demonstrate the importance of a transport process in the over-all sorption phenomenon. The rate of PMG sorption was noted to increase markedly as the degree of agitation in the PMG-pulp system was increased. No such dependence could have been found for an adsorption-controlled reaction.

In summary, therefore, the sorption of PMG from solution by sulfite pulp fibers is hypothesized to involve two steps — a transport process and adsorption proper at the fiber surface. In view of these studies,

the transport process is concluded to be the important rate-determining factor in the over-all sorption phenomenon.

THE NATURE OF PMG SORPTION ON SULFITE PULP FIBERS

In earlier sections of this thesis, as experimental results were presented and discussed, the principal emphasis has been on the rate aspects of PMG sorption. In addition, however, these studies permit a consideration of the nature of the sorption phenomenon itself. It seems appropriate therefore, in this section, to unify these findings in a composite hypothesis describing the mechanism of PMG retention.

Pertinent to this discussion is an analysis of the variation in the rate of PMG sorption as a function of time. Such rate relationships may be determined from the sorption-time curves shown in Figure 4 on page 42 of this thesis. The sorption-time curves of Figure 4 are described by the equation, $\underline{x}/\underline{M} = \underline{K}\underline{t}^{\underline{n}}$, where $\underline{x}/\underline{M}$ is the PMG specific sorption, $\underline{t}$ the time, and $\underline{K}$ and $\underline{n}$ constants. The constants $\underline{K}$ and $\underline{n}$ may be evaluated by plotting the data on logarithmic coordinates, and then determining the slope and intercept. By differentiating the sorption time equations, the rate relationships for the sorption process may be determined. These are presented in the footnote to Table XXI and were used to calculate the data for the rate-time curves plotted in Figure 13. Details of the development of these rate relationships are presented in Appendix V.

It will be noted in Figure 13, that the rate of PMG sorption, initially high, decreased very sharply and then began to level off at a much lower

TABLE XXI

RELATIONSHIP BETWEEN RATE OF PMG SORPTION AND TIME

Pulp Fraction C-II, 11,780 sq.cm./g.
Pulp Consistency, 0.0167%
Temperature, 25°C.
pH, 6.5

Initial PMG Concn., g./l.	Time, sec.	Calculated Rate of PMG Sorption x 10^5, g./g. pulp per sec.
0.100[a]	6	11.8
	12	7.7
	18	6.0
	30	4.4
	60	2.9
	120	1.9
	300	1.1
	600	0.7
	900	0.5
0.050[b]	6	9.4
	12	6.2
	20	4.5
	30	3.6
	60	2.3
	100	1.7
	300	0.9
	600	0.6
	900	0.4
0.025[c]	6	4.5
	12	3.1
	18	2.6
	30	2.0
	60	1.4
	120	0.9
	300	0.6
	600	0.4
	900	0.3
0.0125[d]	6	3.2
	12	2.3
	18	1.9
	30	1.5
	60	1.1
	120	0.8
	300	0.5
	600	0.4
	900	0.3

TABLE XXI (Continued)

Initial PMG Concn., g./l.	Time, sec.	Calculated Rate of PMG Sorption x 10^5, g./g. pulp per sec.
0.005[e]	6	1.9
	12	1.4
	18	1.1
	30	0.9
	60	0.6
	120	0.4
	300	0.3
	600	0.2
	900	0.2

a $R_{0.100} = 3.5 \times 10^{-4}\ t^{-0.62}$
b $R_{0.050} = 2.8 \times 10^{-4}\ t^{-0.61}$
c $R_{0.025} = 1.1 \times 10^{-4}\ t^{-0.51}$
d $R_{0.0125} = 7.5 \times 10^{-5}\ t^{-0.48}$
e $R_{0.005} = 4.8 \times 10^{-5}\ t^{-0.51}$

t = time, sec.

value. Since infinite bath conditions were approached throughout the course of the sorption runs, it is improbable that this decrease in rate was caused by a reduction in the concentration of PMG in solution. Rather, this behavior suggests that more than one process may be involved in the retention of PMG as the sorption phenomenon continues with time.

A similar observation is noted from the relationship between sorption rate and the amount of PMG retained on the fiber. This relationship is presented in Figure 14. When plotted in this manner, in contrast to the curves in Figure 13, the very sharp reduction in the rate of PMG sorption is not observed. Rather, the reduction in rate tends to follow a smooth curve and then levels off as the concentration of PMG on the fiber increases. The shape of these curves suggests an exponential

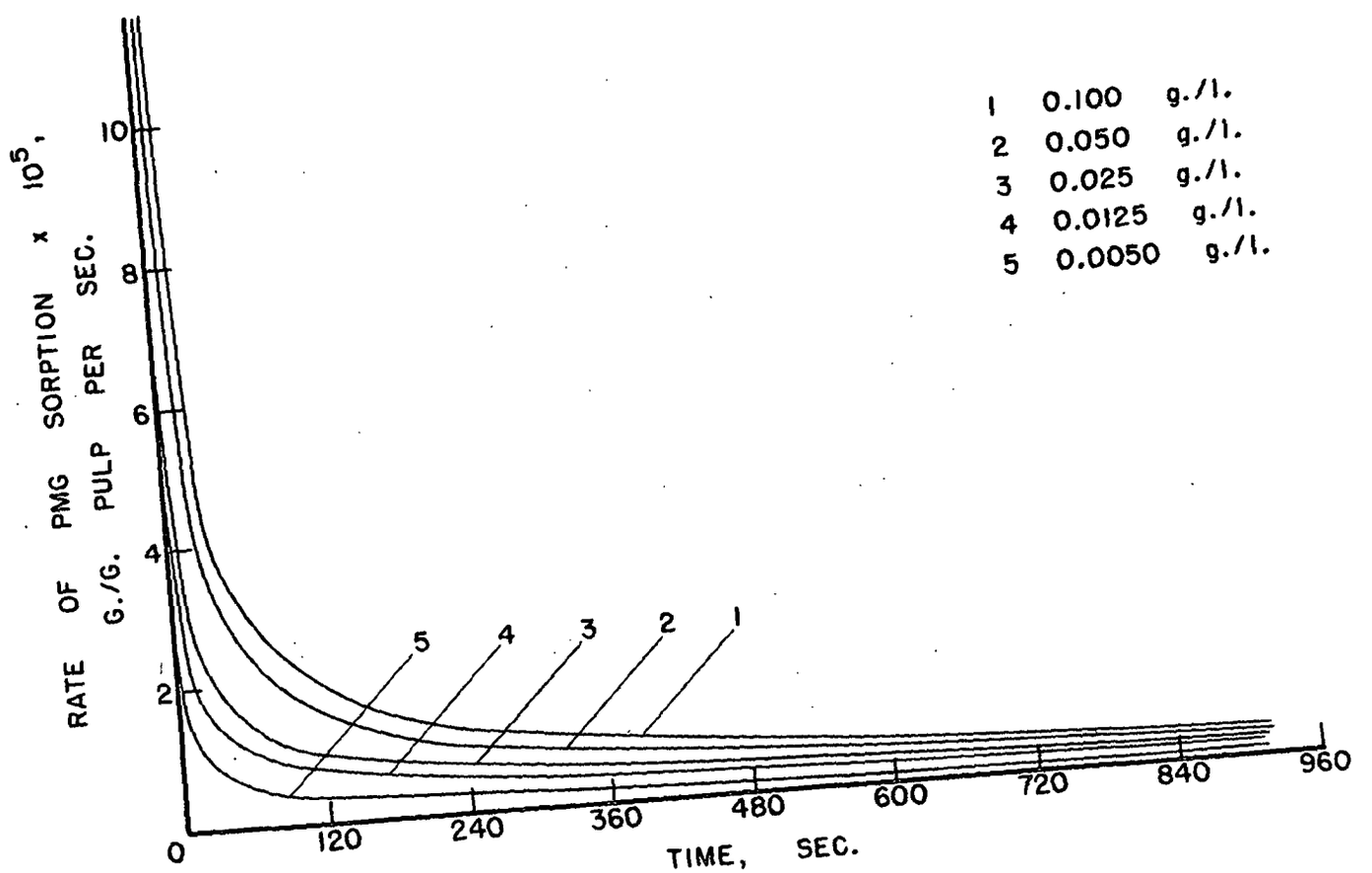

Figure 13. Rate of PMG Sorption as a Function of Time on Pulp C-II

decrease in PMG sorption rate possibly resulting from multilayer sorption of the PMG.

A further indication of possible multilayer PMG sorption may be cited. Based on estimated dimensions of the PMG polymer, and the surface area of the pulp fibers, one may calculate the amount of PMG theoretically required to form a monolayer at the liquid-fiber interface. For these calculations, the PMG polymer was assumed to be an oblong ellipsoid, as reported for LBG by Kubal and Gralén (18), with a width of 51 A., a length of 255 A., and a molecular weight of 310,000. These dimensions represent a very conservative estimate of the size of the PMG molecule. Assuming a parallel arrangement of the PMG molecules at the fiber surface, as little as 5 mg. of PMG per gram of pulp would be sufficient to cover the surface of the fibers of Pulp C-II used in this study. This level of PMG retention was achieved early in the sorption runs at the higher concentration levels, namely at 0.050 and 0.100 g./l. Consequently, as sorption continued, it appears that sufficient gum was retained in these experiments to correspond to a multilayer PMG sorption phenomenon. While it must be realized that this calculation is only an approximation, the order of magnitude involved indicates that gum to gum-fiber sorption may be taking place.

Tentatively, the view taken here is that throughout the cellulose there exist numerous "active centers", probably associated with the individual molecules, which are responsible for an attractive force between the PMG and the cellulose. Once within the force field, these centers are capable of attracting and holding the PMG molecule.

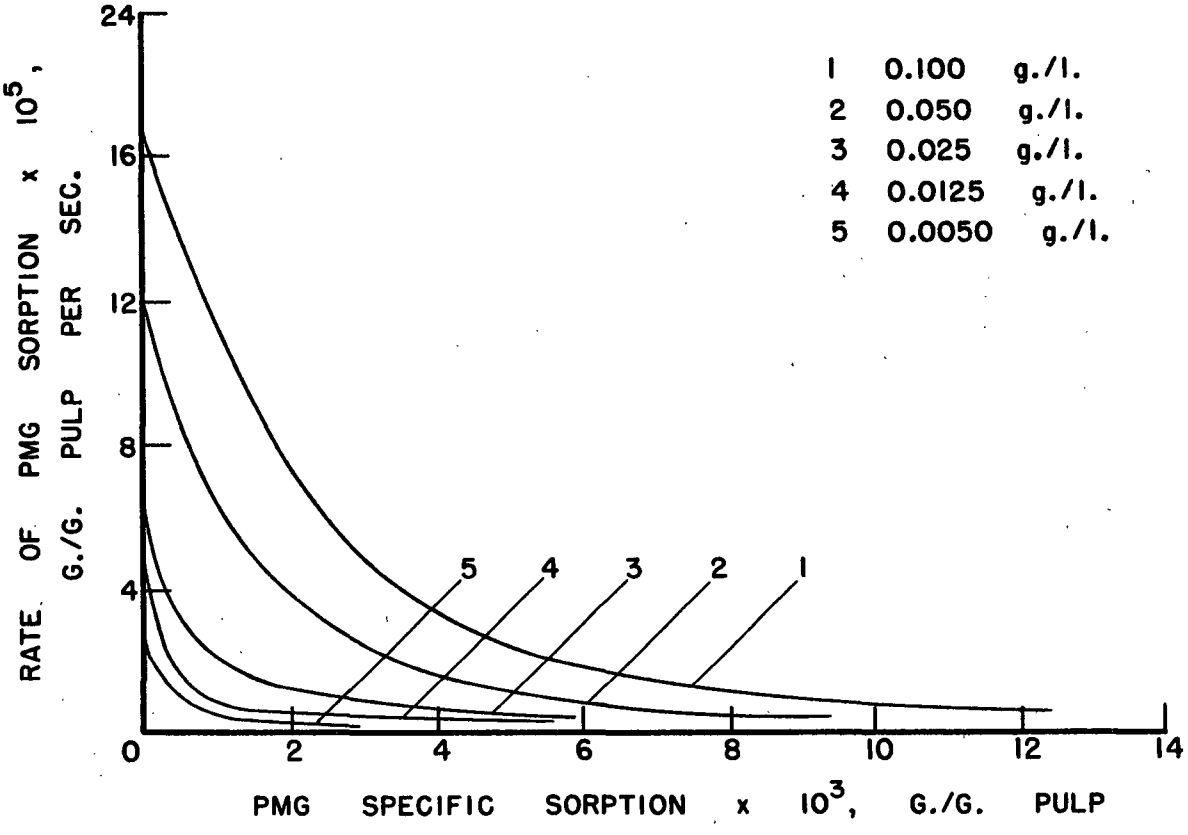

Figure 14. Relationship between Rate of PMG Sorption and PMG Specific Sorption on Pulp C-II

These attractive forces would set up an attractive field which may be assumed to be an inverse power function of the distance from an active center. With these physical attractive forces, the activity of an active site is not considered terminated by the adsorption of PMG, but only reduced. Initially, with the fiber surface uncovered, the attractive forces would be at a maximum and the sorption rate at its highest level. As the surface thickness of gum is built up, and the gum to gum-fiber process becomes predominant, the initial attractive force would be reduced, and the sorption rate decreased.

This hypothesis does not assume a total and uniform coverage of the fiber with PMG prior to further sorption. Because of the rapid initial sorption, a more random orientation probably exists, with free fiber surfaces available for further sorption. These surfaces, however, would be less accessible to subsequent PMG molecules in solution because of the partial blocking effect of adjacent sorbed molecules. Thus, the rate of sorption at these sites would also proceed more and more slowly as the amount of sorbed PMG increased.

In this hypothesis, retention of the PMG is suggested to occur via multiple hydrogen bonding. Both the pulp fiber and the molecules of gum are strongly hydrophilic and rich in electronegative groups. According to Pauling (41), these groups form hydrogen bonds relatively easily. Since a large number of potentially active groups exist on both the fiber and gum, an attachment between one point on a gum molecule and the surface enhances the possibility of bonding between neighboring groups of the same molecule and the surface. In this way, multiple hydrogen bond formation

is possible, resulting in a high degree of sorption irreversibility. For desorption of the gum, many such bonds would have to be broken and a very high energy of activation would be required for this reverse reaction. The order of magnitude of this energy requirement would have to be many times that of the 4400 cal./mole noted for the initial rate of sorption. Consequently, in this sense, the ultimate retention of the gum may be seen to involve energies of the order of chemisorption phenomena. At the present time, direct calorimetric determinations of the heat changes accompanying the desorption process are not possible.

As an objection to the multilayer PMG sorption hypothesis advanced above, mention should be made of the possibility of an alternate mechanism of sorption; namely, one involving the retention of aggregates of PMG molecules. While the possibility of such a sorption phenomenon cannot be overlooked, its occurrence in the present study is believed to be unlikely. However, in the absence of direct experimental evidence, such as in the form of osmotic pressure measurements, the exclusion of such a possibility cannot be established unequivocally.

The belief that an aggregation phenomenon is unlikely results from the following considerations. The PMG molecule, as a mannogalactan derivative, consists of a linear chain of D-mannose units with side chains of D-galactose on about every third or fourth mannose unit. Such side chains allow the mannogalactans to become highly hydrated by association with a large envelope of water molecules. Further, Whistler (42) states that in solution these protruding galactose units tend to fend off one gum molecule

from another or at least produce such irregularities that extensive interchain association cannot take place. This action prevents the formation of aggregating particles which would bring about precipitation, and thus disperse molecules remain stable. In the present research, great care was exercised in the preparation of clear PMG stock solutions free from any detectable undispersed gum. These solutions were extremely stable, and on long standing exhibited no turbidity or other evidence of aggregation.

In summary, therefore, a multilayer retention mechanism is hypothesized for the sorption of PMG by the pulp fibers in this research. It is suggested that this phenomenon is a consecutive rate process, involving both deposition of gum on the fiber, and subsequent sorption of gum by the gum-fiber complex. The sorption process, requiring a low energy of activation, is believed to be of the physical or van der Waals type. Physical dispersion forces from numerous "active centers" throughout the cellulose surface are suggested as setting up a force field capable of attracting and holding the PMG molecule. Ultimate retention of the gum is hypothesized to occur via multiple hydrogen bonding, resulting in a high degree of sorption irreversibility.

SUMMARY

Studies of the sorption of PMG (a partially methylated derivative of locust bean gum) on a bleached sulfite pulp, with especial consideration of the rate-determining factors, were performed in an effort to elucidate the nature of the over-all sorption process. These studies were approached from an initial rate standpoint under "infinite bath" sorption conditions. Retention of the sorbed gum was determined directly by means of a radiochemical tagging technique.

Based on an analysis of the PMG-pulp system, two steps were postulated as the important rate-determining factors in the over-all sorption phenomenon. These were first, a transport process, and second, adsorption proper at the fiber surface. The sorption experiments of this research were designed to provide an insight into the relative importance of each of these factors. Experiments were conducted to investigate the effect on the rate of PMG sorption of the variables time, PMG concentration, temperature, degree of agitation, and pulp specific surface area.

The observed temperature dependence of the initial rate of PMG sorption showed a low temperature coefficient. For each 10°C. rise in temperature, the initial rate of sorption was increased by a factor of 1.3. The order of magnitude of this figure is consistent with a physical process as rate-determining in the over-all PMG sorption phenomenon. The nature of such a process was elaborated by a consideration of the calculated energy of activation for the initial rate of PMG sorption. The figure of 4400 cal./mole was strongly suggestive of a diffusional transport process,

adsorption of the van der Waals type, or a combination of both these processes as rate-determining. Further, since the value 4400 cal./mole reflects the rate-determining step in the over-all process, the adsorption step per se cannot require a greater energy of activation. Consequently, the adsorption step must occur at a rate in excess of or comparable in magnitude to that of the transport process.

The importance of a diffusional transport step was investigated further by studying the effect of agitation on the sorption of PMG. The initial rate of PMG sorption was noted to increase markedly as the degree of agitation in the PMG-pulp system was increased. At 3000 r.p.m., the initial rate of sorption was as much as 35% greater than that of the reference control run. No such dependence on agitation could have been found for an adsorption-controlled reaction. It was suggested that the tangential shearing stresses accompanying stirring reduces the resistance to molecular transfer, and thus enhances the transport of PMG to the fiber surface.

In view of these studies a transport diffusional process was concluded to be the important rate-determining factor in the over-all PMG sorption phenomenon.

In addition to the major conclusion that a transport process is rate-determining in the over-all PMG sorption phenomenon, these studies made possible a hypothesized characterization of the sorption process itself. Studies of the effect of time on the sorption of PMG by pulp fibers showed that the retention of PMG increased with increasing contact times.

The rate of sorption was initially high, decreased very rapidly, but continued at a finite level. When the concentration level was maintained, the sorption of PMG did not reach a condition of equilibrium rapidly, and sorption equilibrium was not achieved in 112 hours. A multilayer retention mechanism was hypothesized for the sorption of PMG by the pulp fibers in this research. It was suggested that this phenomenon is a consecutive rate process, involving both deposition of gum on the fiber, and subsequent sorption of gum by the gum-fiber complex.

SUGGESTIONS FOR FUTURE RESEARCH

The following recommendations for additional research are suggested in an effort to further elucidate the sorption behavior of polysaccharide beater adhesives.

1. The nature of the PMG transport phenomenon should be investigated in greater detail. Attempts should be made to determine diffusion coefficients for the adhesive-pulp system. In addition, efforts should be made to include mixing parameters in such a study.

2. In the over-all sorption phenomenon, efforts should be made to study the nature of the adsorption process per se in greater detail by reducing or eliminating the diffusional transport resistances in the gum-fiber system. An approach to such a condition may obtain from the use of very high concentrations of gum, or sorption studies in a system with high rates of shear.

3. An investigation of the role of pulp fiber fines in the sorption of beater adhesives is recommended. Fines are known to possess an enormous surface area, and special emphasis should be placed on the competition between sorption on this material and the longer, more defined, whole-fiber fractions.

4. The effect of hydrolysis on the sorption characteristics of mannogalactan gums should be investigated. Both mild and drastic

conditions of hydrolysis are suggested. This would permit studies of the importance of the branched side chains in the polymer, and should also contribute to our understanding of polymer D.P. in relation to sorption.

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APPENDIX I

PREPARATION AND ANALYSIS OF PULP

PULP BEATING

For the sorption studies in this research, a Weyerhaeuser standard bleached sulfite pulp was beaten in a laboratory Valley beater for intervals of 20, 35, 50, and 75 minutes. At each interval, two 360-gram batches of pulp were prepared. For each beater interval, the procedure was as follows.

A pulp charge of 360 grams (oven-dry basis) was diluted with 10 liters of filtered tap water and soaked overnight. The soaked pulp was disintegrated in a Williams stirrer for 5 minutes with the propeller 3 inches from the bottom of the container. Halfway through the disintegration the stirrer was stopped, and the stock was mixed by hand to remove any pockets of stock at the edges of the container.

Eight liters of water were added to the beater, at a temperature such that the addition of the disintegrated pulp stock resulted in a final temperature of 25 $\pm$ 2°C. The stock was then circulated for 5 minutes with no load on the bedplate. During this period, additional water was added at 25°C., to give a total of 23 liters in the beater, with the pulp at a consistency of 1.5%.

At the end of this slushing period, 5500 grams were placed on the lever arm and the pulp was beaten for a given refining time. At the end

of each interval, the bedplate load was removed, the beater stopped, and the entire pulp charge dumped.

Two runs were made in this manner for each beating interval. The refined pulp from these runs was mixed thoroughly, dewatered on a large Büchner funnel using Cenco creped No. 13255 filter paper, and then broken up by passing through the laboratory pulp breaker several times. Solids determinations were made. The pulp was stored in double polyethylene bags at 5°C., with 1% formaldehyde as a preservative.

Schopper-Riegler freeness values were determined for each beater interval.

REMOVAL OF FINES

A Bauer-McNett classifier was used for the removal of fines and fiber debris at each beating interval. The classifier was set up with 8, 12, 65, and 150-mesh screens. For each classification charge, 30 grams (oven-dry basis) of pulp were diluted to 2 liters with filtered tap water and disintegrated for 300 counts in a British Disintegrator. This pulp charge was run through the classifier for 15 minutes; the stock through 150 mesh was discarded. At the end of 15 minutes, the contents of the four classifier tanks were combined in a muslin-covered washbox and the classifier thoroughly cleaned. The pulp in the washbox was allowed to drain free to prevent the loss of fibers.

For each beater interval, 10 to 13 classifier runs were made. The classified pulp from these runs was combined, dewatered, and then mixed in

the laboratory pulp breaker. Samples were taken for the determination of solids, and the pulps placed in double polyethylene bags for storage. The pulps were stored at 5°C. with 1% formaldehyde as a preservative.

The yield of classified pulp at each interval was determined. The stock loss represented fines and fiber debris.

APPENDIX II

CALIBRATION OF THE PROPORTIONAL COUNTING TUBES

The tube characteristics of three proportional counting tubes were obtained by determining their counting rate, at a constant level of carbon-14, as a function of the total carbon content, over a range of voltages.

A series of four solutions of sodium carbonate were prepared. Each solution contained identical amounts of radioactivity, nominally 1920 d./m. per ml., but ranged in total carbon content from 1.4 to 6.0 mg. per ml. Two-milliliter aliquots of each solution were analyzed for their total carbon contents manometrically in the Van Slyke apparatus. The liberated carbon dioxide was then transferred to each of the proportional tubes for counting.

The results of the manometric carbon analyses are given in Table XXII and demonstrate the reproducibility of this technique. The data for the counting rate as a function of the applied voltage for each of the tubes and at four levels of total carbon content are summarized in Table XXIII.

From the data of Table XXIII, smooth curves of counting rate versus applied voltage were drawn for each tube at the four levels of total carbon content. These curves established the counting plateau, and from them an operating voltage for radioactive counting was selected. Examples of the type of curves obtained are shown in Figures 15 and 16 at two carbon loading levels. By counting at 3700 volts, within the counting plateau, the

TABLE XXII

PROPORTIONAL COUNTING TUBE CALIBRATIONS
MANOMETRIC CARBON ANALYSES

Solution	Carbon Content, mg. Tube E	Tube F	Tube G	Average 3 Tubes	Theoretical
I	2.804	2.855	2.840	2.833	2.855
II	6.248	6.298	6.283	6.276	6.339
III	7.645	7.684	7.681	7.670	7.832
IV	11.97	11.98	12.06	12.00	12.14

proportional tube characteristics are such that, up to 7 mg. carbon, essentially the same counting rate is obtained for each of the tubes. The counting rate data taken from all the curves of the type of Figures 15 and 16 at 3700 volts are summarized in Table XXIV.

The effect of total carbon content on the efficiency of counting a constant amount of carbon^{14} was determined by plotting the counting rate of the three tubes as a function of their total carbon content. These curves are presented in Figure 17.

In Figure 17, it will be noted that the counting rate is constant up to 7 mg. carbon, and then the efficiency decreases as has been previously reported by Van Slyke et al. (13). Since in this thesis research, the range of carbon analyzed was in the range from 2 to 4 mg., the drop-off in counting efficiency at higher levels of carbon content is not significant.

TABLE XXIII

COUNTING RATE (c.p.m.) AS A FUNCTION OF TUBE, VOLTAGE AND TOTAL CARBON CONTENT

(Level of radioactivity constant at ca. 3840 d./m.)

Voltage, kilovolts	Counting Rate, c.p.m.								
	Total Carbon 2.833 mg.			Total Carbon 6.276 mg.		Total Carbon 7.670 mg.			Total Carbon 12.00 mg.
	Tube			Tube		Tube			Tube
	E	F	G	F	G	E	F	G	E
3.0	2731	3315	3173	3112	2065	3029	2664	2210	1357
3.1	3099	3599	3480	3441	2567	3338	3166	2756	1924
3.2	3397	3719	3622	3713	2971	3562	3457	3178	2452
3.3	3557	3845	3752	3735	3367	3636	3613	3431	2795
3.4	3691	3873	3816	3841	3588	3812	3833	3621	3099
3.5	3738	3833	3881	3900	3645	3890	3862	3784	3352
3.6	3809	3901	3855	3852	3817	3863	3860	3790	3565
3.7	3786	3895	3950	3913	3826	3882	3858	3798	3616
3.8	3910	3944	3859	3985	3873	3884	3895	3866	3890
3.9	4068	4023	3882	4009	4034	3901	3921	3866	3951
4.0	4290	4041	3930	4077	4167	3962	3978	3986	4242
4.1	4691	4014	4032	4245	4727	4118	4036	4207	4814
4.2	5105	4222	4012	4524	5395	4162	4094	4499	5430
4.3	6013	4476	4122	4876	----	----	4413	----	----

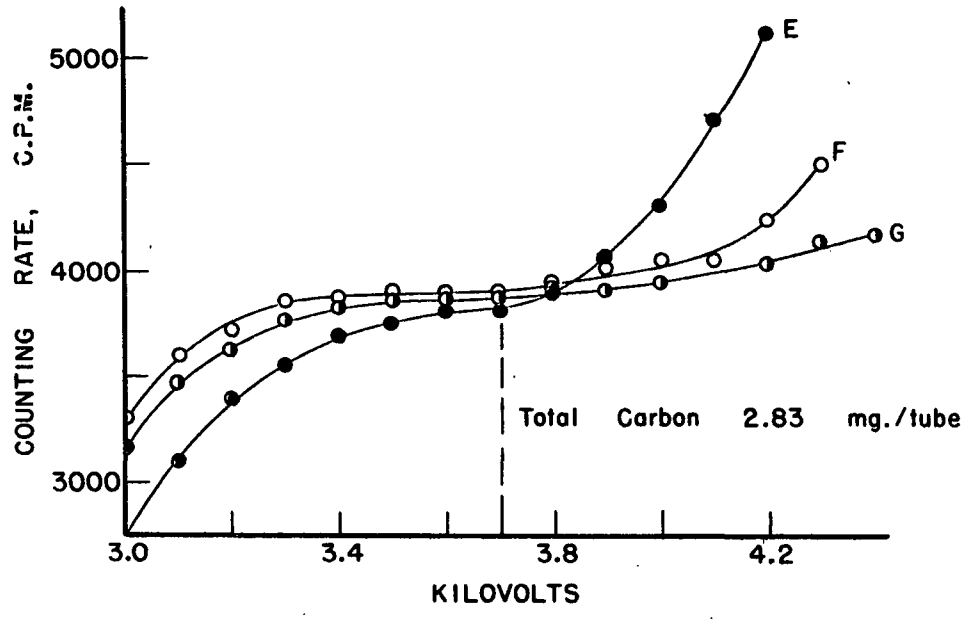

Figure 15. Proportional Counting Tube Characteristics -- Counting Rate versus Voltage

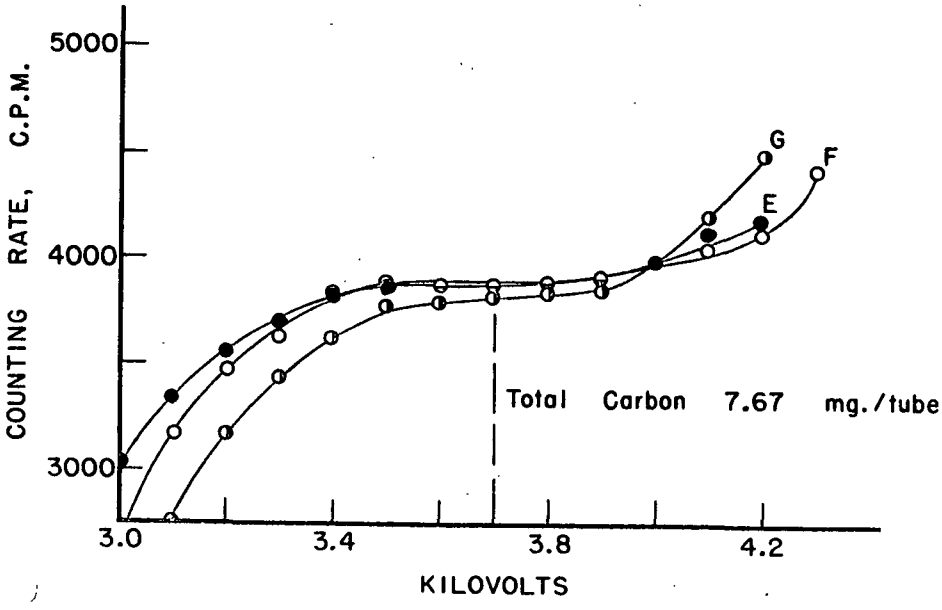

Figure 16. Proportional Counting Tube Characteristics — Counting Rate versus Voltage

TABLE XXIV

CALIBRATION DATA FOR COUNTING TUBES

COUNTING RATE (c.p.m.) AT 3.7 KV.

	Counting Rate, c.p.m.		
Carbon Content, mg.	Tube E	Tube F	Tube G
2.833	3885	3925	3885
6.276	----	3925	3835
7.670	3825	3875	3825
12.00	3616	----	----

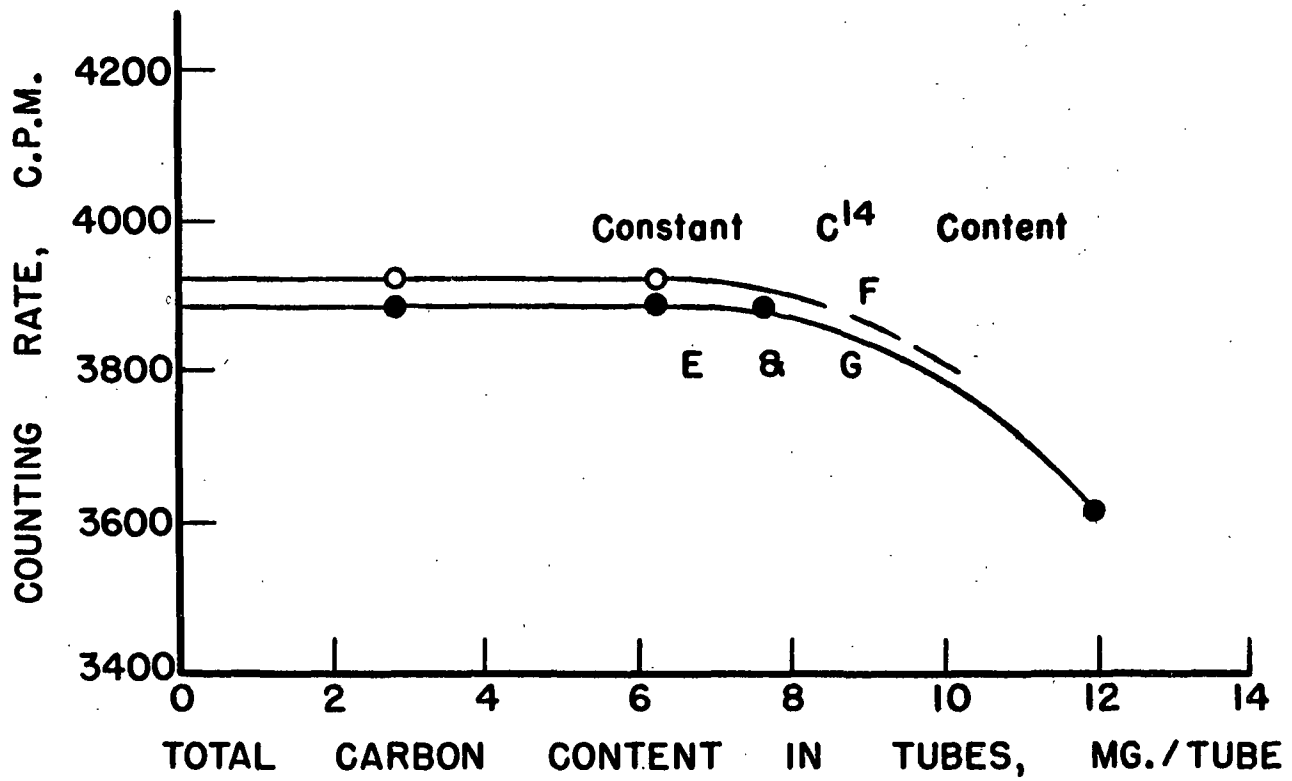

Figure 17. Counting Rate versus Carbon Content in Proportional Counting

APPENDIX III

LABELING LBG WITH CARBON^{14}

LABELING TRIALS WITH CARBON^{14} SODIUM CYANIDE

Experimental: Labeling Trial I

A series of small-scale experiments were performed to determine the cyanide combining power of the prepared purified LBG. Approximately 100-mg. samples of LBG were reacted with carbon^{14} sodium cyanide at two levels of LBG concentration, 0.5 and 1.0%, and with double and four times the theoretical cyanide present. At 1.0%, the solution of LBG was not clear, and swollen, undissolved LBG remained in suspension. The theoretical amount of NaC^{14}N necessary was estimated from the data of Isbell (11).

The reaction was allowed to proceed for two weeks at room temperature, and was then continued at 60°C. for four hours. After hydrolysis of the cyanohydrins, the reaction mixtures were poured into vigorously stirred 95% ethanol to precipitate the LBG. The 1.0% LBG samples were lost during this precipitation step. On pouring into ethanol, the original swollen undissolved LBG formed tough, gelled masses. The LBG in the 0.5% solutions was successfully recovered by precipitation into 95% ethanol. This precipitated product was redissolved in hot water, the solution was cooled, and the gum reprecipitated into 95% ethanol. It was then solvent dried with absolute ethanol followed by absolute ether.

The specific activity of the labeled LBG products was determined by

oxidizing samples to carbon dioxide, and measuring the radioactivity by proportional counting. From these measurements, the specific activity of the labeled LBG, its cyanide combining power, radiochemical yield, and apparent D.P. were calculated. These results are presented in Table XXV.

TABLE XXV

$NaC^{14}N$ LABELING TRIAL I

	Reaction Conditions[a]	
	0.5% LBG Excess $NaC^{14}N$, 200%	0.5% LBG Excess $NaC^{14}N$, 400%
Specific activity, mμc./mg.	9.9	7.5
Calculated combining power, mmol. $NaC^{14}N$/g.	0.0018	0.0014
Radiochemical yield, %	1.5	1.1
Apparent D.P.	3300	4400

[a] Excess in reaction conditions based on data of Isbell (11), i.e. 0.0307 mmol. HCN/g.

Both the specific activity and the radiochemical yield of these labeled products were much lower than anticipated. Based on the work of Most (5), a labeled product with a specific activity of 30 mμc/mg. was expected, with a radiochemical yield of about 20%. Although low, the specific activity of the labeled LBG would have been adequate for use as a radioactive tracer, provided a greater quantity of gum were tagged. The reaction efficiency however was very poor, and the yield of 1% prohibitive. Under these conditions, the loss of radioactive $NaC^{14}N$ was

too great to be practicable. The low values of calculated combining power suggested that the purified LBG contained only a small number of reducing end groups. On this basis, the excess cyanide present at the start of the labeling reaction was much greater than the twofold and fourfold amounts which were desired. These large excesses may have been responsible for the low radiochemical yields which were obtained.

Experimental: Labeling Trial II

In an effort to improve the radiochemical yield, another series of small-scale labeling experiments was conducted. These experiments were based on both the newly determined cyanide combining power of the first labeling trial, and the original value reported by Isbell (11). Also included in these experiments was a direct comparison between the $NaC^{14}N$ used in the first trial, and the $KC^{14}N$ used by Most (5) in the labeling of slash pine hemicelluloses. Since these radioactive cyanides were obtained from different suppliers, it was believed that possibly the untested $NaC^{14}N$ did not meet its reported specificiations. Experiments were performed with an excess of cyanide and also with an excess of LBG. In addition, in two of the trials sodium bicarbonate was included in the reaction mixtures as a buffer. All the experiments were run with LBG concentrations of 0.5%.

The reaction was allowed to proceed for two weeks at room temperature, and then was continued at 60°C. for four hours. The precipitation procedure used for the recovery of the labeled LBG was a modification of that followed in the first labeling experiments. Instead of pouring the

reaction mixtures into 95% ethanol, the procedure was reversed, and the ethanol was poured into the vigorously stirred reaction mixture. This modification was found to produce a less stringy, more flocculent LBG which subsequently was easier to centrifuge and purify. The precipitated LBG was purified as described above, by redissolving in hot water and reprecipitating with 95% ethanol, followed by solvent drying with absolute ethanol and absolute ether.

The radioactivity of this series of labeled products was determined by counting in the solid phase with a Geiger-Müller tube. It was impossible to use proportional counting in the gas phase because liquid nitrogen, a necessary component in the Van Slyke (24) technique, was not available at the time. It should be emphasized, therefore, that the data obtained were only of limited value. They are sufficiently reliable for a relative evaluation within the series of experiments, but cannot be used for absolute considerations. An attempt was made to calibrate the Geiger-Müller counting with a sample of labeled LBG of known specific activity; however, there is no assurance that the geometry of counting remained exactly the same in every case. From the sample of known activity the efficiency of the Geiger-Müller counting was estimated as about 8%, but it could have varied between 5 and 10% (25). The results of these labeling experiments are presented in Table XXVI.

While it was necessary to treat the results of this labeling trial with caution, certain conclusions could be made. The $NaC^{14}N$ labelings were not as effective as those with the $KC^{14}N$ of Most (5). Although the

TABLE XXVI

CYANIDE LABELING TRIAL II

Reaction Conditions	Radio-activity Added, mμc./mg.	Calculated Specific Activity, mμc./mg.	Calculated Combining Power, mmol. $NaC^{14}N$/g. ($sl0^4$)	Estimated Radio-chemical Yield, %
D.P. 200[a] Excess $NaC^{14}N$, 400%	660	3.7	6.9	0.6
D.P. 3000[b] Excess $NaC^{14}N$, 400%	50	0.2	0.4	0.4
D.P. 200[a] Excess $KC^{14}N$, 400%	390	5.9	19	1.5
D.P. 3000[b] Excess $KC^{14}N$, 400%	30	0.4	1.2	1.5
D.P. 200[a] Excess LBG, 25% $KC^{14}N$	70	2.1	6.7	2.8
D.P. 3000[b] Excess LBG, 25% $KC^{14}N$	5	0.1	0.3	2.4
D.P. 200[a] Excess $NaC^{14}N$ 300% $NaHCO_3$[c]	500	5.6	10.4	1.1
D.P. 3000[b] Excess $NaC^{14}N$, 300% $NaHCO_3$[c]	40	1.5	2.7	3.6

[a] D.P. 200 - theoretical combining power based on data of Isbell (11), i.e. 0.0307 mmol. HCN/g.

[b] D.P. 300 - theoretical combining power based on Labeling Trial I, i.e. 0.0020 mmol. HCN/g.

[c] For each mmol. NaCN, one mmol. $NaHCO_3$ added.

amount of activity believed to be present in the $NaC^{14}N$ experiments was about 1.6 times that of the $KC^{14}N$ trials, the latter produced products which were about 1.6 times more active than those of the former. A check of the activity of both stock solutions of cyanide showed the $NaC^{14}N$ to be twice as radioactive as the $KC^{14}N$. This was in accord with the specified radioactivity contained in each stock solution. However, from the labeling trials, it appeared that the radioactivity in the stock solution of $NaC^{14}N$ was not all present as cyanide. The stock solution was returned to its supplier for a more complete characterization, and only a portion of the radioactivity present was found to be in the form of $NaC^{14}N$. This explains in part the poor results of Labeling Trial I, but yet does not resolve the problem completely.

The results of the radiochemical yield data, and the calculated cyanide combining powers were perplexing. As in the first labeling trial, the radiochemical yields were very low. While not strictly comparable to the yields of the first trial, it is significant to note that within this series no marked differences in yield were obtained. This was true even with the labelings based on a very low combining power. Possibly a mass action effect entered into the reaction, but it is difficult to conceive that it would be of such significance.

The variation in the calculated combining powers was even more puzzling. One would expect these values to be relatively constant. This variation, and the low radiochemical yields suggests the possibility that little true cyanohydrin synthesis occurred. If this were the case, much

of the observed radioactivity of the LBG products may have resulted from the sorption of radioactive material from the reaction mixture.

Experimental: Hydrolysis and LBG Combining Power

In an effort to increase the combining power of the LBG, without major alterations in the molecule, the effect of a mild hydrolysis on the gum was investigated.

The conditions for the hydrolysis were determined from a viscometric study in a spot experiment. Mild conditions were desired with little change in the LBG molecule, and the use of viscosity measurements provided a convenient means for studying the variables of the hydrolysis. Into a no. 200 Ostwald-Fenske viscometer were placed 10 ml. of a 0.25% solution of LBG containing 2% sulfuric acid. The viscometer was suspended in a 25°C. water bath and the change in viscosity, in terms of the efflux time, was noted over a period of 85 hours. These data are presented in Table XXVII.

The viscosity measurements in Table XXVII indicated that a broad range of hydrolysis products could be obtained by increasing the time of hydrolysis. Based on these data a series of hydrolyses were run with 2% sulfuric acid at room temperature. These hydrolyses were continued for 0, 8, 16, 24, 36, 48, and 72 hours, respectively. The solutions were neutralized with barium carbonate or barium hydroxide, and after filtering off the precipitate of barium sulfate, the hydrolyzed LBG products were recovered by precipitating into 95% ethanol. The recovered products were

TABLE XXVII

EFFECT OF 2% H_2SO_4 ON LBG VISCOSITY

Time, hr.	Efflux Time, sec.	Decrease, %
0	70.0	—
12	56.0	20
16	51.5	25
24	46.5	33
37	39.0	44
64	31.0	56
85	27.0	62

solvent dried with absolute ethanol and anhydrous ether to prevent hornification.

Alkaline hypoiodite was used to determine the combining power of the hydrolyzed LBG products. The technique employed was essentially that of Martin, et al. (26), modified for use at the greater dilutions necessary in this study. Although good results were obtained in the calibration experiments with samples of glucose, no reducing or combining value could be determined for the series of hydrolyzed LBG products. Evidently, the conditions of hydrolysis were too mild to affect the main chain of the LBG molecule to any significant extent. The effect of the hydrolysis on the viscosity probably resulted from cleavage of galactose side chains from the principal mannose chain, rather than being due to any great scissioning of the main chain itself. Whistler (27) reported that the branch chains

of mannogalactans are much more readily susceptible to hydrolysis than the main chain.

Initially, further hydrolysis trials with differing reaction conditions were to be performed with the LBG in an attempt to increase its combining power. However, these trials were not made for a number of reasons. They would have been too time-consuming, and conditions sufficiently severe for satisfactory hydrolysis undoubtedly would have drastically shortened the LBG molecule. In view of this situation, it was considered more prudent to label LBG with carbon^{14} by employing the alternate methylation technique of Swanson, Becher, and Dickey (7).

LABELING BY METHYLATION WITH CARBON^{14} METHYL IODIDE

Preparation of Sodium Salt of LBG

Ten grams of purified LBG and 180 ml. of freshly prepared 2N ethanolic NaOH were refluxed for 4 hours at 83°C. After refluxing, the sodium alcoholate of LBG was washed four times with successive portions of 95% ethanol. This product was then stored moist in a tightly sealed bottle prior to subsequent methylation with carbon^{14} methyl iodide.

Methylation with Carbon^{14} Methyl Iodide

A special apparatus, designed to reduce the loss of carbon^{14} methyl iodide, was constructed for the radioactive methylations. It consisted of two 50-ml. round-bottomed flasks, and two condensers connected by a glass tube. This permitted recovery of the residual carbon^{14} methyl

iodide from a reaction in the first flask. The residual methyl iodide was distilled over to the second flask for a second methylation.

For Labeling Run I, approximately 1.5-g. samples of the sodium alcoholate of LBG were placed in each of the reaction flasks. The ampoule of carbon^{14} methyl iodide, containing one millicurie of radioactivity, was cooled in dry ice and acetone until the methyl iodide solidified. The tube was broken open carefully, and the methyl iodide was dissolved in a small portion of a solution composed of 0.75 ml. inactive methyl iodide as a carrier, and 9 ml. of 95% ethanol. The reaction mixture was transferred quantitatively to the first reaction flask with successive portions of the inactive solution.

This methylation mixture was refluxed for 8 hours at 81-3°C., with well water at 5°C. circulating through the condensers. After refluxing, the reaction was stopped, the condenser was drained, and the residual methyl iodide and ethanol were distilled over into the second flask. An additional 2 ml. of 95% ethanol, and 0.4 ml. of inactive methyl iodide were added and the second reaction mixture was also refluxed for 8 hours. Both products were washed five times with acetone, dried *in vacuo* at 33°C., and subsequently purified as described below.

The procedure of Labeling Run I was modified for the second labeling series. The carrier solution was added in two portions, and the residual reaction mixture was further distilled from the second flask to a third one. Approximately 3 g. of the sodium alcoholate of LBG were placed in the first flask, 2 g. in the second, and 1 g. in the third. At the start

of the reaction, one millicurie of carbon^{14} methyl iodide was transferred to the first reaction flask with a solution of 6 ml. of 95% ethanol and 0.55 ml. of inactive methyl iodide. A further addition of 0.6 ml. of inactive methyl iodide and 12 ml. of 95% ethanol was made 15 minutes later.

As in Labeling Run I, the reaction mixture was refluxed for 8 hours followed by distillation of the residual methyl iodide and ethanol to the second reaction flask. An additional 0.7 ml. of inactive methyl iodide was added, and the refluxing procedure repeated. After refluxing for 8 hours, the unused methyl iodide and ethanol were distilled in the third flask, 0.5 ml. of inactive methyl iodide was added, and a final methylation performed. The products were washed five times with acetone, and dried *in vacuo* at 33°C., prior to purification.

Purification of Methylated LBG Products

The crude partially methylated products were purified by resolution and precipitation. The gums were dissolved in vigorously stirring distilled water at 0.5% concentration. Where necessary, gentle heating on a steam bath was used to dissolve the products. After cooling, the pH of the solutions was adjusted to neutral with a few drops of 5% acetic acid. The gums were then precipitated by pouring slowly into 95% ethanol. The alcohol volume was 2.5 times that of the gum solution. The products were collected by centrifuging, washed five times with absolute ethanol, and three times with acetone. Finally, the gums were dried *in vacuo*, over magnesium perchlorate, at 55°C.

The products LBG-Ia and LBG-Ib, from Labeling Run I were purified separately. Similarly, from Labeling Run II, product LBG-IIa was treated separately, while the products LBG-IIb and LBG-IIc were combined before purification.

APPENDIX IV

THE SORPTION BEHAVIOR OF MIXTURES OF METHYLATED AND UNMETHYLATED LBG

EXPERIMENTAL DESIGN

The sorption characteristics of nonradioactive unmethylated LBG, in mixture with a radioactive methylated product, cannot be determined directly from radioactivity measurements. For a direct study of the behavior of the unmethylated gum, an independent method for retention, such as that used by Leech (6) would be necessary. Such an approach would be involved and tedious, and for the purposes of this work it was believed that sufficient knowledge about these sorption characteristics could be determined indirectly. Here, the chief interest was in whether or not preferential sorption occurred when a mixture of the two gums is added to a pulp sample. If there is no preferential sorption, then the calculated retention of these mixtures, as determined from radioactivity measurements, will be independent of the amount of the radioactive component present.

To study such an effect, equal amounts of a series of gum mixtures containing different ratios of radioactive methylated gum were added to equal quantities of pulp. Two experimental runs were made containing a total gum content of 1% based on the pulp. In Run 1 the ratio of methylated to total LBG varied from 4.75 to 100%, while in Run 2 the composition was varied from 4.97 to 75%. Individual sorption solutions were made up in 8-oz. wide-mouthed jars, and then pulp, which had previously

been broken up in a malted milk mixer for 30 seconds, was added. The final concentration of the pulp in the sorption medium was 0.5%. Run 1 was performed at 27°C., with the samples agitated by a conventional propeller-type stirrer. Run 2 was conducted at 24°C., and agitated less vigorously by rotating the samples in the jars end over end. Each sorption run was continued for one hour and the individual pulp samples were recovered by filtering on a coarse fritted-glass funnel. The samples were immediately washed with two 500-ml. portions of distilled water, and finally dried in a vacuum desiccator with calcium chloride.

The retention of the radioactive LBG was determined from wet combustions with the Van Slyke technique (24). From these analyses and the ratio of radioactive methylated to total gum, the percentage of LBG sorption was calculated. The raw data are presented in Table XXVIII and plotted in Figure 18.

ANALYSIS OF DATA

In Figure 18, for both runs, it will be noted that the calculated total LBG retention varied with the amount of radioactivity present. Apparently, therefore, there is a preferential effect in the sorption of mixtures containing methylated and unmethylated LBG. The unmethylated nonradioactive LBG appears to be sorbed to a greater extent than the methylated radioactive product. Had there been no preferential sorption, the plotted data would have resulted in a horizontal straight line.

It may also be noted in Figure 18 that the sorption curve tends to

TABLE XXVIII

RAW DATA — SORPTION OF MIXTURES OF METHYLATED AND UNMETHYLATED LBG ON BLEACHED SULFITE PULP

	Composition, Radioactive/Total LBG, %	Radioactive LBG Added, mg./100 g. pulp	Radioactive LBG Determined, mg./100 g. pulp	Calculated Total Retention, %
Run 1	4.75	47.5	30.6	64.7
			30.7	64.5
	16.5	165	97.1	58.8
			96.2	58.3
	33.3	333	174	52.3
			173	52.1
	50.0	500	271	53.1
			259	51.9
	75.0	750	353	47.3
			364	48.6
	100.0	1000	478	47.8
			479	47.9
Run 2	4.97	49.7	27.8	58.5
	9.96	99.6	52.0	52.0
	16.5	165	88.5	53.5
	25.5	255	122	48.8
	75.0	750	333	44.5

level off above a composition of 50% radioactive to total LBG. Because of this effect, it was at first believed that perhaps the curvature in the low range was not real, but a result of insufficient sensitivity due to experimental errors. In this range, where the percentage of radioactive gum is low, the calculation for total sorption would greatly multiply the

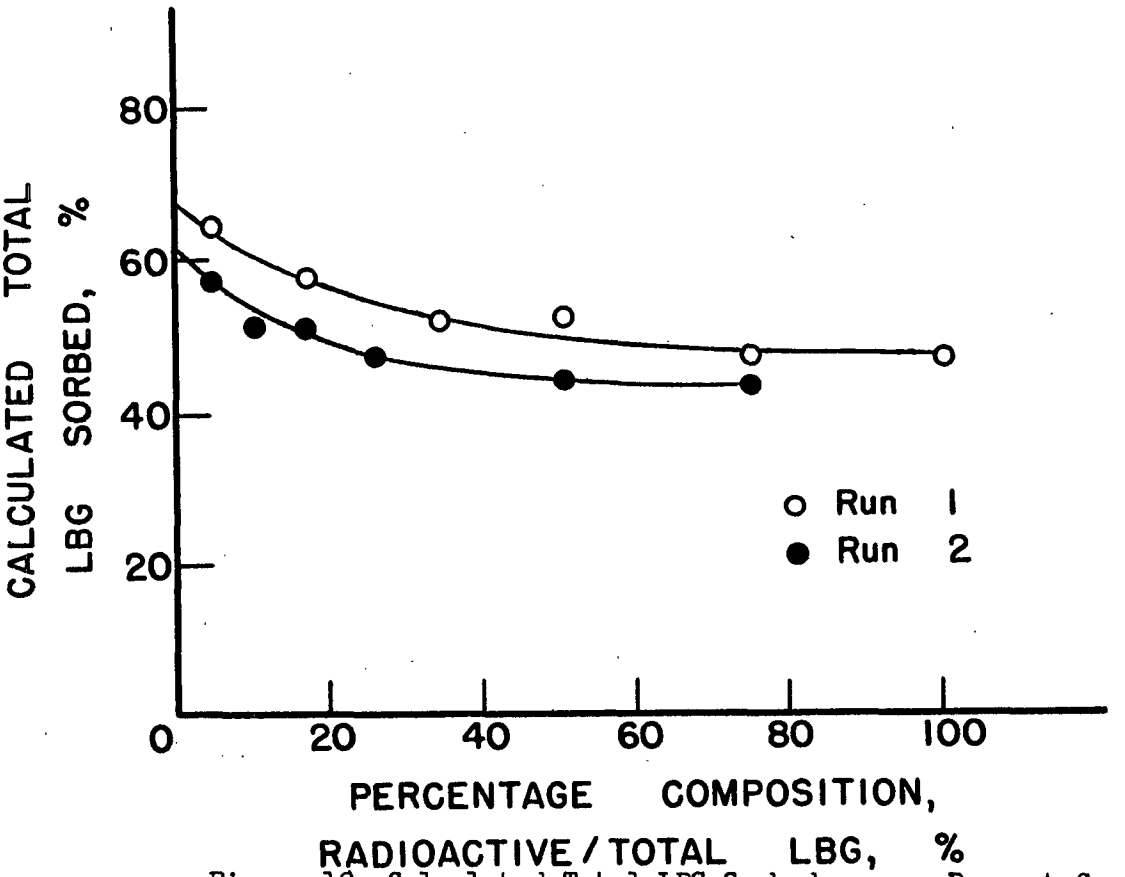

Figure 18. Calculated Total LBG Sorbed *versus* Percent Composition — Raw Data

effect of small errors. To minimize the effect of such possible errors, the data were smoothed on the basis of the actual radioactive LBG retention measurements. This was accomplished for both runs by plotting the amount of determined radioactive LBG *versus* the radioactive LBG which had been added, drawing the line of best fit through this data. These curves are shown in Figure 19. From them, corrected retention values for the retention of radioactive gum were obtained. These data are tabulated in Table XXIX and plotted in Figure 20.

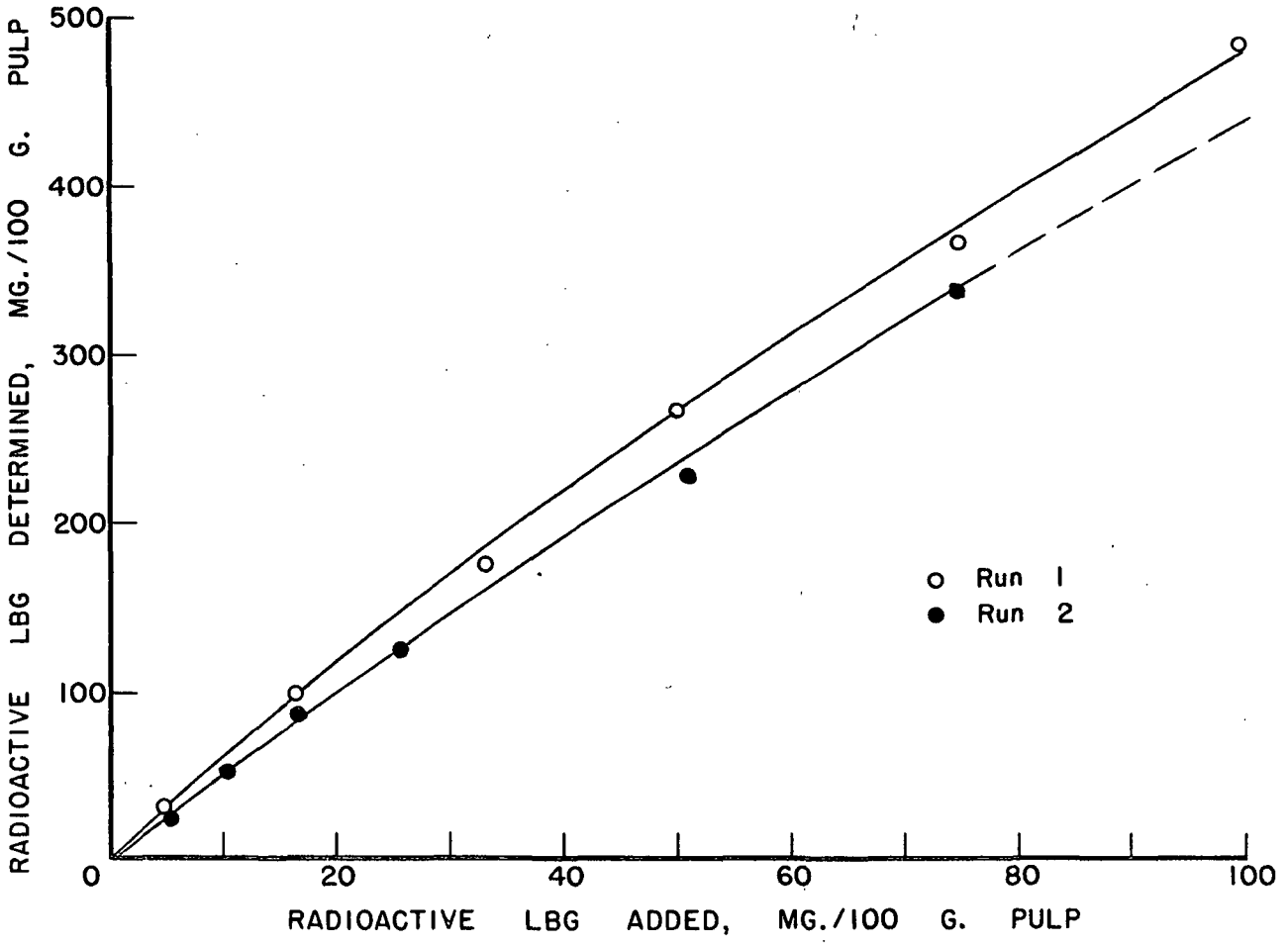

Figure 19. Radioactive LBG Determined versus Radioactive LBG Added

TABLE XXIX

SMOOTHED DATA — SORPTION OF MIXTURES OF METHYLATED AND UNMETHYLATED LBG ON BLEACHED SULFITE PULP

	Composition, Radioactive/Total LBG, %	Radioactive LBG Added, mg./100 g. pulp	Radioactive LBG Determined, mg./100 g. pulp	Calculated Total Retention, %
Run 1	4.75	47.5	26	54.7
	16.5	165	90	54.6
	33.3	333	174	52.0
	50.0	500	255	51.1
	75.0	750	370	49.4
	100.0	1000	483	48.3
Run 2	4.97	49.7	27	54.4
	9.96	99.6	52	52.3
	16.5	165	83	50.3
	25.5	255	125	49.1
	51.0	510	235	46.1
	75.0	750	336	44.8

Once again, it will be noted, that the curves of calculated percentage LBG sorption versus percentage composition of the radioactive LBG are neither straight nor horizontal lines. Smoothing the data has reduced the extent of curvature but a definite sorption curve still results, indicating preferential sorption.

On the basis of these data, it seems reasonable to conclude that a true preferential sorption effect has taken place, the curve of which

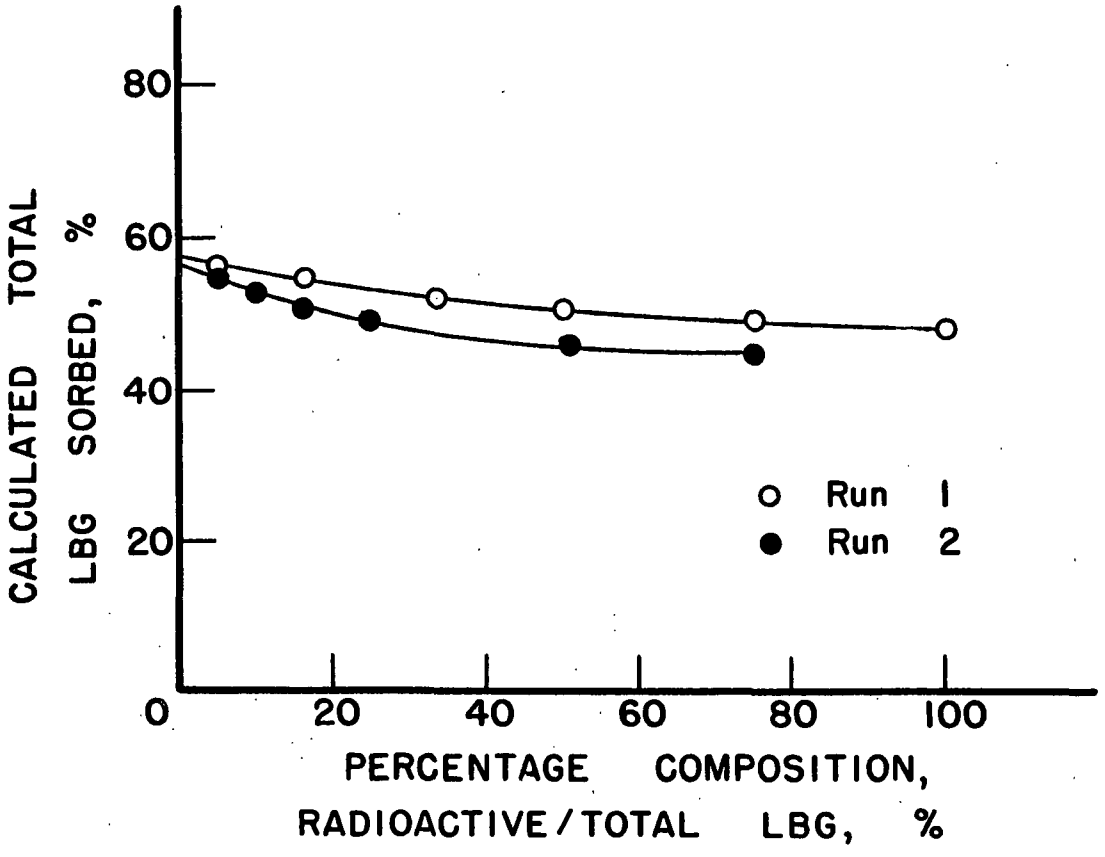

Figure 20. Calculated Total LBG Sorbed versus Per cent Composition Smoothed Data

probably lies somewhere between the raw data of Figure 18, and the smoothed data of Figure 20. It is interesting to note that a horizontal straight line (indicative of no preferential sorption) will be obtained from a plot of calculated LBG sorbed versus percentage composition only when the function relating the determined radioactive LBG versus the added radioactive LBG is a straight line passing through the origin. This may not be immediately obvious, but results from the fact that with equal amounts of total LBG, the abscissas of the two graphs described above are equivalent. In Figure 19 there is some scatter to the data, but the indicated trend is

that of curves and not straight lines. The good precision of the duplicate analyses of Run 1 are strong evidence that the data, though limited, are reliable.

Further evidence of differences in the nature of methylated and unmethylated LBG was obtained from the strength properties of handsheets containing these gums. At the same level of LBG addition, sheets made with the unmethylated gum had burst and tensile strengths 7% greater than those made with the methylated product. The sorption conditions for these sets of sheets were identical, but the retention could not be determined. In view of the above data on sorption this difference in strength may have resulted from differences in retention of the two gums.

APPENDIX V

CALCULATIONS

CALCULATION OF PMG RETENTION

The manometric carbon analysis of Van Slyke *et al.* (24), followed by proportional counting of the carbon^{14} radioactive products provides a simple, straightforward method for determining the retention of polysaccharide beater adhesives on samples of pulp fibers or paper. This method is especially convenient inasmuch as there is no need to determine the sample size independently prior to the radioactive determination for the adhesive. In the PMG-pulp system of this study, the sorption of PMG per unit weight of fiber was calculated from the following formula:

$$\frac{x}{M} = \frac{K_1 \, (r/a)}{(\Delta p)(F) - (r/a)K_2}$$

where: $\frac{x}{M}$ -- mg. PMG per mg. pulp fiber

K_1 -- constant, percentage carbon in pulp fiber

r -- c.p.m., determined by proportional counting

a -- specific activity of PMG, c.p.m./mg.

Δp -- pressure of carbon dioxide evolved in Van Slyke combustion at a definite volume and temperature

F -- factor, multiplied by Δp gives total carbon in milligrams

K_2 -- constant, percentage carbon in PMG

For a given sorption experiment, with a stock solution of known activity, a , this technique involves the measurement of only the variables

Δp, the pressure of the evolved carbon dioxide, and r, the c.p.m. of the radioactive carbon^{14}.

DEVELOPMENT OF RATE RELATIONSHIPS

The sorption-time data of Table XII, as plotted in Figure 4, appeared to be power functions. Such sorption isotherms may be described by the equation, $x/M = kt^n$, where x/M is the PMG specific sorption, t the time, and K and n are the constants. Equations of this type when plotted on a log-log basis produce straight line relationships with slope n, and intercept k. Thus, the constants n and k may be evaluated.

By subsequent differentiation of these sorption isotherms, expressions may be obtained for the rate of sorption as a function of time. For the parabolic isotherms described here, the rate expression becomes $d(x/M)/dt = nkt^{n-1}$.

This procedure was applied to the data of Table XII. A log-log plot of the data is presented in Figure 21. From the slopes of these lines, the constants, n were determined at each level of PMG concentration. With n known, the intercepts k were evaluated by substitution of corresponding values of x/M and t in the expression,

$$\log x/M = n \log t + \log k$$

and then solving for k. The rate relationships were then obtained from the sorption isotherms by differentiation as described above. These expressions are presented in the footnote to Table XXI.

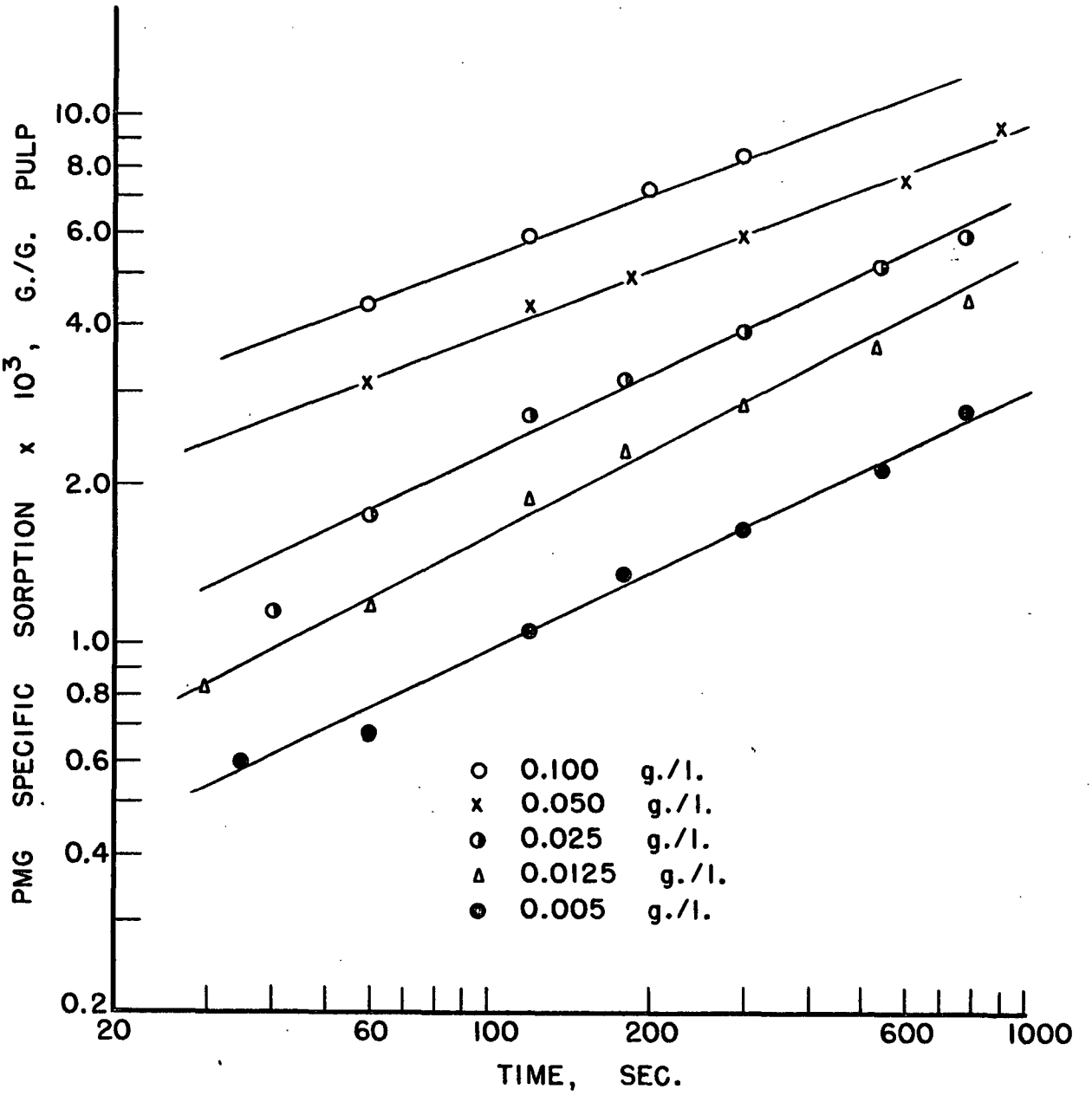

Figure 21. Effect of Time and Concentration on PMG Sorption